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(30) MICROCAPSULE, TREATMENT LIQUID CONTAINING MICROCAPSULES, AND TEXTILE STRUCTURE  
HAVING MICROCAPSULES STUCK THERETO.

② This invention relates to a microcapsule having a particle diameter of 2 to 300  $\mu\text{m}$  and comprising at least such substances as acting to improve physiological conditions of human skin, for example, substances exhibiting such effects as skin whitening, aging preventive, humidity preservative, itch suppressive, pain-killing, or antiphlogistic ones, and/or aromatic agents contained within the filmy coating of synthetic high molecular substance thereof. The microcapsule is not broken when making, processing, or laundering the textile structure, however, is gradually broken when the textile structure is put on the human body, used for the other purpose, or subjected to intentional application of friction or pressure thereto, and releases acting substances contained therein. Treatment liquid comprising such microcapsules and binder, preferably containing spraying agent, adapt the microcapsules to tightly stick to textile structures as stocking, underwear, and bedclothes, thereby providing a textile structure to exhibit the aforesaid effects.

## [TECHNICAL FIELD]

The present invention relates to microcapsules encapsulating a substance having a function to improve physiological conditions of human skin, such as vitamin C, vitamin E, seaweed extracts, antipruritics and analgesics, and/or aromatic agents; treating liquids containing such microcapsules; and textile structures treated with such a treating liquid, particularly apparel which are worn contacting directly with human skin, such as stockings, socks, underwear or the like, bedclothes or medical auxiliary materials.

## [Background art]

Hitherto in the cosmetic field, etc., there have come into the market articles with the object of skin whitening, such as whitening creams, whitening packs or the like, namely, cosmetics incorporated with vitamin C (ascorbic acid) efficacious against melanopathy and can maintain a fair and fresh complexion by protecting the skin against speckling, freckling or the like. There also have been placed on the market articles with an object of moisturizing the skin, such as humidity preservable creams, humidity preservable packs or the like, namely, cosmetics incorporated with alga colloid, i.e., a seaweed extract, as an active principle having a moisturizing effect to prevent drying of the skin, which could realize a soft, young and fresh skin by moisturizing the skin.

Thus, recently, importance is being attached to the skin-care of hands and feet equally to the faces, so that whitening lotions or the like incorporated with vitamin C or seaweed extracts have appeared for application to arms or legs.

However, lotions or creams such as the above-mentioned type to be left as they have once been applied to the surface of the skin are directed to use after bathing, before sleeping or the like, which have not given a certain sustained function to the skin. Accordingly, it is the present situation that generally skin-care from going out in the morning until coming home has not been taken into consideration.

Pharmaceuticals with an object of analgesic, antiphlogistic or antipruritic have so far been developed in diversified dosage forms such as internal medicine, injection, ointment or plaster, and many have been placed on the market. For example, in Japanese Patent Application Laid-open No. 60-188,314 are described antipruritic plasters comprising an ointment compounded with crotamiton as an antipruritic active principle, and in Japanese Patent Application Laid-open No. 60-178,837 are described oral-administrable gelatine capsules encapsulating an anti-SRS-A agent.

However, these administration methods have not always been effective, as one feels uncomfortableness inherent in ointments when one has no plain nor itch, one cannot be given selectivity in acting position, or fast-acting effects when one feels pain or itch, feels uncomfortableness and harm inherent in injection, or the like. Further, as technology to utilize microcapsules, there have been proposed: a method of applying a mixture of microcapsules encapsulating a liquid toilet preparation with a size containing a melamine resin to textile articles (British Patent Specification No. 1,401,143); a method for preparing fragrant towel fabrics by applying a liquid mixture of aromatic-containing microcapsules with an acrylic resin to towel fabrics (Japanese Patent Application Laid-open No. 58-4,886); a process for preparing fragrance-emitting printed articles, by printing a printing paste comprising microcapsules composed of a filmy starch envelope encapsulating an aromatic agent, a thermoplastic material and a thickening agent (Japanese Patent Applications Laid-open Nos. 53-47,440 and 53-49,200); and the like. However, there have not yet been disclosed microcapsules encapsulating the above-mentioned material functionable to improve physiological conditions of the skin, such as vitamins, seaweed extracts, analgesics, antipruritics or the like (hereinafter, may be referred to as "skin-improver").

Further, as a hitherto proposed pillow having a fragrance, there have been those having a pillow-case coated with a resin containing an aromatic agent or those with a sachet or scent paper attached thereto.

In Japanese Patent Application Laid-open No. 61-63,716, there has been also proposed a fragrant core and sheath type composite filament comprising a core incorporated with a dispersion of an aromatic agent and having a cavity in the core. However, there has been a problem such that the aromatic agent is prone to volatilize or deteriorate at a high temperature, so that aromatic agents endurable melt-spinning are limited. Alternatively, application by transfer-printing method, as disclosed in Japanese Patent Application Laid-open No. 53-106,885, also cannot provide sufficiently a long-lasting fragrance. Further, problems also have arisen such that the binder permeates into woven or knitted yarns, resulting in a very stiff hand, or the transfer-printed portions have a different hand and are detached by washing, etc. Namely, the above-mentioned fragrant pillows have had a serious drawback such as poor resistance to washing. In order to enhance the resistance to washing, it is required to increase the amount of resin coating, wherefore the

hand of the pillow cases has been considerably impaired.

[Disclosure of invention]

5 A principal object of the present invention is to improve very naturally and continuously physiological conditions of the skin.

Another object is to provide apparel, particularly such as stockings, underwear or the like, which contacts directly with the skin and gradually releases a skin-improver by movement or action of the human body while it is worn, to give a long-lasting, whitening, humidity preserving, pain-killing, antipruritic or the like effect to the skin.

10 Further another object is to provide textile fabrics, or made-up articles or laminated sheet materials thereof which can attain "pain-killing or antipruritic effect when required".

A further different object is to provide a treating liquid containing a skin-improver or an aromatic agent which is excellent in resistance to washing and, further, a spray of the treating liquid containing a propellant.

15 The above-described objects can be achieved by a microcapsule characterized by encapsulating at least a substance having a function of improving physiological conditions of human skin, having a particle diameter within the range of 2-300  $\mu\text{m}$  and being composed of a wall membrane comprising a synthetic high molecular material.

The above-mentioned substance is preferably at least one skin-improver selected from the group consisting of ascorbic acids, tocopherols, seaweed extracts, analgesics and antipruritics.

20 The above-mentioned synthetic high molecular material comprises preferably a formaldehyde resin as a main component.

The present invention includes a treating liquid characterized by containing microcapsules encapsulating a substance having a function of improving physiological conditions of human skin and having a particle diameter within the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material, and a binder, at a weight ratio of 10:1-1:5.

Such a treating liquid can be a spray containing a propellant.

The above-mentioned binder contained in the treating liquid of the present invention is preferably a silicone based resin or urethane based resin.

25 The present invention further includes textile structures characterized by having microcapsules encapsulating a substance having a function of improving physiological conditions of human skin and having a particle diameter within the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material, adhering thereto with a binder, a weight ratio of said microcapsules to said binder being in the range of 10:1-1:5 and the total amount of said microcapsules and said binder adhering to the structure being 0.3-15% based on the weight of fibers in the adhering portion.

Typical textile structures of the above include stockings.

Additionally, underwear is also important as the textile structure of the present invention.

As another embodiment of the present invention, mention may be made of a textile sheet characterized in that a first textile fabric having the microcapsules adhering thereto is laminated on a second textile fabric or sheet.

30 A further different embodiment of the present invention is a microcapsule characterized by encapsulating an aromatic agent and having a particle diameter within the range of 5-30  $\mu\text{m}$  and a wall membrane comprising a formaline based resin as a main component.

Such a microcapsule encapsulating an aromatic agent can be mixed with a resinous binder at a weight ratio of 10:1-1:5 to prepare a fragrance processing liquid.

40 This processing liquid is preferred to be applied in the form of a spray further containing a propellant.

As ascorbic acids to be employed in the present invention, mention may be made of any known compounds comprising ascorbyl palmitate, ascorbyl stearate, ascorbyl dipalmitate, ascorbic acid phosphate magnesium salt, or the like. Particularly, ascorbyl dipalmitate is preferred in respect of whitening effect and feasibility in microencapsulating, which has a good dermotic absorbability and high safety for skin, acts effectively as an ascorbic acid source and has been generally utilized as a material for compounding medicated cosmetics for which physiological effects of ascorbic acids are expected.

45 As tocopherols to be applied to the present invention, mention may be made of  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol and  $\delta$ -tocopherol, which function to restrain aging of the skin that is otherwise accelerated by peroxide lipid as well as to activate skin and also to prevent melanosis.

The seaweed extracts to be employed in the present invention are to mean, for example, those obtained by extracting dry powder of the genus *Laminaria* belonging to the class Phaeophyceae with JSCl purified water and adding JSCl 1,3-butylene glycol thereto. The laminaria contains abundant vitamins,

proteins and saccharides, in addition to minerals, such as calcium, phosphorus, iodine or the like, and is generally known to function to enhance humidity preserving action and metabolism.

As antipruritics to be employed in the present invention, mention may be made of known compounds, such as clemizole sulfate, isothiopendyl hydrochloride, diphenhydramine and its derivatives, hydrocortisone, prednisolone and its homologues, fluorometholone, flucinolone acetone, formocortol, fludrocorticide, fluocinonide, flumetasone pivalate, triamcinolone, dexamethasone, betamethasone valerate, beclometasone dipropionate, guiazulene, crotamiton, camphor, zinc white, indometacin, flufenamic acid, ibuprofen or the like. These are used alone or in combination.

As analgesics to be employed in the present invention, mention may be made of known pharmaceuticals to be used for muscle ache, contusion ache, neuralgia and stiffness, such as salicylic acid derivatives, such as methyl salicylate or the like, tocopherol acetate, diphenhydramine and its derivatives, zinc oxide, l-menthol, camphor, or the like. These are used alone or in combination.

As an aromatic agent to be employed in the present invention, mention may be made of benzoin, cypress oil, ilang-ilang oil, fennel oil, neroli oil, chamomile oil, cardamon oil, clary sage oil, black pepper oil, cedar wood oil, jasmine oil, juniper oil, camphor, geranium oil, oilbanum oil, basil oil, patchouli oil, rose oil, hyssop oil, sandalwood oil, pennyroyal oil, peppermint oil, bergamot oil, marjoram, melissane, myrrh, eucalyptus oil, lavender oil, rosemary oil and the like. For pillows, the jasmine oil, rose oil and sandalwood oil are preferred.

The wall membrane of the microcapsule according to the present invention is composed of a synthetic high molecular material comprising, as a main component, a thermosetting resin such as a formaline based resin, a polyester resin or the like (at least 50% by weight), preferably a urea-formaline based resin, a melamine-formaline based resin, and excellent in resistances to heat, pressure and water. Other than the above, acrylic resins (usable in combination with a cross-linking agent such as methylene-bis-acrylamide, divinyl compounds or the like), vinyl chloride based resins and cellulosic resins also can be used. The particle diameter of the microcapsule is generally within the range of 2-300  $\mu\text{m}$ , and when it adheres to fiber, it is preferred to be within the range of 4-40  $\mu\text{m}$  that is smaller than the diameter of single fiber. Particularly when an aromatic agent is contained or the microcapsules adhere to stockings, the range of 5-20  $\mu\text{m}$  is preferred. Further, these microcapsules are preferred to withstand pressure or friction during processing or washing, and to have such a strength that the microcapsules may be broken or cracked little by little after adhering to textile articles, when the textile articles are worn or by an intentional friction.

Alternatively, the percent of the wall membrane is generally 3-60 weight % based on the weight of the microcapsule and when the microcapsule is made to adhere to fiber, it is preferred to be within the range of 5-50 weight %. Particularly when it is made to adhere to a stocking, the range of 5-25 weight % is preferred.

Furthermore, the percent of the aromatic agent contained is 10-90 weight % and the thickness of the membrane is 0.3-4  $\mu\text{m}$ , preferably 0.5-2  $\mu\text{m}$ .

The composition of the microcapsule containing a skin-improver to be employed in the present invention is not specifically limited insofar as the microcapsule breaks to release the skin-improver by the action of an appropriate friction as mentioned above. However, low-formaline microcapsules are preferred.

The above-described microcapsules can be manufactured by known processes, such as an *in situ* polymerization process, an interfacial polymerization process or the like (for example, as disclosed in A. Kondo, "Microcapsules" in the Industrial Technology Library 25, published by Nikkan Kogyo Shimbusha, 1970, and Japanese Patent Application Publication No. 7724/1962). In the case of a formaline based resin wall membrane, a core component material compounded with at least a skin-improver or aromatic agent and urea or melamine are emulsified in water (using, as an emulsifier, sodium sulfonated polystyrene, polyodium acrylate, acrylic acid copolymer, maleic acid copolymer, polyvinyl alcohol, polyethylene glycol or the like, preferably at least acrylic acid copolymer or maleic acid copolymer particularly when the core component material comprises l-menthol or peppermint oil; conducting pH control if required; and at a water temperature of 40 °C), then a formaline aqueous solution is added and the temperature is elevated to 70 °C while agitating, to conduct polycondensation reaction. Then, the produced microcapsules are filtered and dried to obtain the microcapsules containing a skin-improver or aromatic agent according to the present invention. Additionally, the size is controlled mainly by agitation power and concentration of the emulsifier, the percentage of the wall membrane is controlled mainly by concentration of urea or melamine in oil droplets and the porosity of the wall membrane is controlled mainly by concentration of formaline (in order to make it dense, highly concentrated formaline is used). Furthermore, in order to dissolve or dilute the skin-improver, alcohols such as decyl alcohol, lauryl alcohol, glycerine or the like, esters such as lauryl stearate, palmitic acid glyceride or the like, natural oils such as peppermint oil, tsukabi oil, soybean oil, sesame oil, rape oil, coconut oil, clove oil, turpentine oil, beef tallow, eucalyptus oil or the like, can be

incorporated additionally as a core component material (in this case, those incompatible with the wall membrane of the microcapsules should be selected).

The textile structures referred to in the present invention include yarns, staples, woven or knitted fabrics, nonwoven fabrics and secondary articles thereof, which may be composed of natural fibers, regenerated cellulosic fibers, synthetic fibers or mixtures thereof by blend spinning, plying, mix spinning, hybrid knitting or weaving, or the like. In connection with adhesion of binders, fibers having a rough surface, such as cotton, microporous fibers having microvoids or the like, or fibers having a compatibility with the binders are advantageous. The textile fabrics may be known fabrics such as woven, knitted or nonwoven fabrics or the like. Alternatively, as a sheet material, in addition to known films such as polyethylene films, 10 polypropylene films or the like, papers including synthetic papers can be used.

Furthermore, the fibers to be employed in the present invention are preferred to be subjected in advance to a water-repelling pretreatment to prevent permeation of binders into knitting or weaving yarns or interstices of fabrics to stiffen the hand, so that the binder and microcapsules may adhere mainly to the surface of the fabrics and the hand inherent in fibers may not be impaired. As a water repelling treatment, 15 known processes can be adopted. However, in the case of application of the products which requires no water-repellency, they may be only impregnated with a relatively small amount of the treating agent followed by drying. For example, there is mentioned a process wherein an emulsion prepared by admixing aluminum acetate and paraffin with an emulsifier and a protective colloid is incorporated and dried, a process wherein an emulsion prepared by admixing methyl hydrogen polysiloxane with an emulsifier and a metallic soap is incorporated, dried and heat-treated, or the like.

The textile structures treated with a skin-improver according to the present invention can be used as underwear, stockings, socks, pajamas, gauze, bandages, supporters, sheets or tapes laminated with textile fabrics or films, or the like.

The stocking that is a typical textile structure the present invention is applied to is to mean collectively all stockings, such as overknee stockings, full-length stockings up to groin, panty stockings comprising integrally united panty and stocking portions, and the like. Its material may be selected from any of synthetic fibers such as nylon fibers, polyester fibers or the like, and natural fibers such as cotton fibers, or the like. The knitting texture is also not specifically limited.

Further, the clothing to wear directly contacting with skin, such as lingerie, foundation, leotards, T-shirts 30 or the like, and bedclothes to contact with skin, such as mattress covers, sheets, pillows or the like, are also as important in the present invention as the above-described stockings.

As a preferable processing process of such textile structures, mention may be made of a process wherein a treating liquid containing microcapsules encapsulating a skin-improver admixed with a resinous binder is applied to a textile structure, for example, a textile fabric or apparel, subjected in advance to water-repelling pretreatment, by means of soaking, padding, coating, spraying or printing.

The binder is not specifically limited insofar as it is a known resin such as silicone based, urethane based, vinyl acetate based, acrylic based, vinyl chloride based, phenolic based or the like, or a known sizing agent such as processed starch or the like. However, silicone based, urethane based or the like resins forming a rubbery film are preferred in respects of durability and pressure absorability. In particular, 40 the silicone based resinous binders display a coating effect and play a role as an adhesive between microcapsules containing a skin-improver and knitted fabrics and, *inter alia*, a silicone based aqueous emulsion type which is excellent in water-dispersibility and can be diluted readily with water, for example, an emulsion comprising, as a main ingredient, an organopolysiloxane emulsified with an emulsifier, is preferred. This hardens upon removal of water, to form a rubbery film having characteristics of a silicone rubber and exhibits an endurable bonding effect. Among the others, preferred are those which can be further dried and treated at 130°C or less. Additionally, the resinous binders may be either of a solution type or an emulsion type. From the viewpoint of handling feasibility and price, an aqueous emulsion type is preferred. For example, silicone based resins, urethane based resins and vinyl acetate, since they harden upon removal of water to form rubbery films, display an endurable bonding effect and are most preferred.

50 The binder is applied in an amount of 0.1-5 times, preferably 0.2-2 times (by weight) that of the microcapsules and displays a sufficient bonding effect. If it is less than 0.1 time, the binding function extremely decreases, while even if it is applied in an amount of more than 5 times, the add-on percent of the microcapsules does not substantially change, inversely causing a problem in the soft hand of fibers or fabrics, so that it is not preferred. Further, the total amount of both of them adhering usually occupies 0.3-15%, preferably 0.5-5.0% based on the weight of the fibers at the portion they adhere to. Namely, since the microcapsules adhere sufficiently to the fibers by applying a binder such as a silicone based resin or the like at the above-mentioned ratio, if the total amount of both of them adhering is less than 0.3% as specified above, both the skin-improving effect and durability are insufficient, while if it exceeds 15%, it affects the

hand of the fibers and further the skin-improver releasing at one time will function excessively, so that it is not suitable either. Namely, the above-specified adhering amount will satisfy all requirements for providing preferable effects of the skin-improver as well as preferable hand and softness and, besides, the skin-improving effects with an appropriate durability.

- 5      The binders are preferred to be applied onto final products, such as apparel, stockings or the like, which are not further subjected to post-processing. A treating liquid containing a binder such as silicone resins or the like may be coated and dewatered or dried by such a means as not impairing the hand.

As a propellant to be employed in the treating liquid spray of the present invention, liquidized propane or butane, LP gas or the like and mixtures thereof are preferred. The mixing ratio of the propellant to the  
10 above-described emulsion is generally 3:97-20:80 (by weight), preferably 5:95-40:60. For a good spraying condition or ironing, known additives such as surfactants, ironing lubricants, glycols, alcohols or the like can be admixed (ironing or hot air drying is conducted preferably at not higher than 130 °C).

Padding materials to be used for the pillows which are particularly important among the bedclothes according to the present invention are not specifically limited in plastics, fibers, wood chips, buckwheat  
15 chaff and the like, and preferred, however, to be polyethylene hollow tubes for their air permeability.

As a method for applying the microcapsules containing an aromatic agent with a resinous binder to the paddings for the pillows, mention may be made of a soaking method, spraying method, coating method, or the like. When the hollow tubes are used, the spraying method is preferred. In the soaking method, microcapsules adhering in the hollow portions of the tubes do not contribute to emission of fragrance, since  
20 they are not broken, thereby resulting in a low yield. The resinous binders are applied generally in an amount of 0.2-5 times, preferably 0.5-2 times (by weight) that of the microcapsules, to present a sufficient bonding effect.

The pillows according to the present invention emit fragrance as the microcapsules break little by little due to mutual frictions of the padding materials in the pillow, caused by every movement of the head. The  
25 feature lies in sound sleep induced at sleepless time, as the more frequently the head moves, the more microcapsules break. On the other hand, since the microcapsules do not break during storing, the fragrance never emits and vanishes.

#### [Best mode for carrying out the invention]

- 30      Next, explanation will be made by way of an example of the manufacturing process of the above-mentioned skin-improving stockings.

In this manufacturing process, the treatment for applying the microcapsules containing a skin-improver is preferred to be conducted at the time of softening treatment after dyeing and fixing of the stockings, as  
35 an excellent treating effect is exhibited efficiently.

On the outset, microcapsules and a binder at a ratio (by weight) of 10:1-1:5 are fed into a treating machine to prepare a treating bath also containing a softening agent. At this time, each chemical should be fed after having been sufficiently dissolved and diluted in water. Then, when these have been sufficiently homogenized, a buffer agent is introduced. This buffer agent is for controlling hydrogen ion concentration to  
40 set and maintain an optimum pH value. As the buffer agent, mention may be made of various materials, such as those comprising, as a main ingredient, a condensed phosphate, which display an excellent pH buffer ability, or the like. However, it is not specifically limited, insofar as it can set and maintain the pH value of the treating bath within the range of 4-6 by its property and amount of feeding. Namely, owing to the fact that making the treating bath acidic will stabilize the treatment with a binder that is weak for alkalis,  
45 promote the reaction, and so forth, the bonding force is strengthened between the microcapsules and binder as well as between the microcapsules/binder and knitted fabrics, whereby adsorbability is extremely improved. Accordingly, the pH value of the treating bath is made to be less than 6. However, if the pH value is as too low as less than 4, the microcapsules and binder coagulate to form a complex which will cause an uneven adhesion, so that it is not suitable. Accordingly, the pH value of the treating bath should be set  
50 within the range of 4-6, preferably at a target value of 4.5-5.5.

Then, an appropriate amount of stockings is introduced into this treating bath and heat-treated at 20-80 °C. If the treating temperature is lower than 20 °C, a satisfactory treating effect can not be obtained, even if the treating time is extended, while if the temperature is higher than 80 °C, it is neither good for each chemical nor the stocking and causes problems in quality, so that it is preferred to be within the  
55 above-mentioned range, particularly 40-60 °C that is a usual temperature for softening treatment. Further, as for the treating time, though it relates to temperature, a long time does not necessarily provide an excellent treating effect so that about 15-30 minutes are enough.

Now, the thus obtained, treated stockings are forwarded to a subsequent process comprising de-

watering, drying and finish-setting steps and finished articles are produced.

- Preferable embodiments of the present invention will be arranged and described hereinbelow.
- (a) A microcapsule as claimed in claim 2, wherein the ascorbic acid is ascorbyl dipalmitate.
  - (b) A microcapsule as claimed in claim 4, wherein the seaweed extract is an extract liquid of the genus *Laminaria* belonging to the class *Phaeophyceae*, admixed with JSCL 1,3-butylene glycol.
  - (c) A microcapsule as claimed in claim 5, wherein the antipruritic agent is selected from the group consisting of clemizole phosphate, isothiopendyl hydrochloride, diphendryamine and its derivatives, hydrocortisone and prednisolone.
  - (d) A microcapsule as claimed in claim 5, wherein the analgesic agent is methyl salicylate.
  - (e) A microcapsule as claimed in claim 7, wherein the formaline based resin is a urea-formaline based resin or a melamine-formaline based resin.
  - (f) A microcapsule as claimed in claim 1, wherein the particle diameter is within the range of 5-30  $\mu\text{m}$ .
  - (g) A microcapsule as claimed in claim 1, wherein the wall membrane occupies 5-25% by weight of the microcapsule.
  - (h) A textile structure as claimed in claim 14, wherein the binder forms a rubbery film.
  - (i) A textile structure as claimed in claim 14, wherein the binder is a silicone based resin.
  - (j) A textile structure as claimed in claim 14, wherein the substance having a function to improve physiological conditions of human skin includes at least L-menthol to also provide refreshing and cool feeling.

The present invention will be explained more concretely hereinafter by way of example.

In the examples, the test for resistance to washing was conducted according to JIS L 0217, 103 Method, and represented by the frequency until the number of microcapsules adhering decreased to 30% or less of the initial number. The percent and part are by weight unless otherwise specified.

## 25 Example 1

On the outset, microcapsules were manufactured as mentioned below.

Three grams of ascorbyl dipalmitate, 8 g of triglyceride, 9 g of squalane, 6 g of a sodium sulfonated polystyrene and 4 g of urea were added to 300 g of water, pH was controlled at 4.0 and the temperature was elevated to 40 °C under agitation, to emulsify. Then, 10 g of a 30% formaline aqueous solution was added and the liquid temperature was increased from 40 °C to 70 °C over 15 minutes while agitating at 500 rpm with a laboratory stirrer. Maintaining the temperature at 70 °C for 60 minutes, a polycondensation reaction was carried out. The produced fine particles were separated from the mother liquid by a glass filter and washed with water. Then, after drying in air, heat treatment at 105 °C was conducted for one minute.

The obtained microcapsules had a particle diameter of 7-15  $\mu\text{m}$  (averaging 10  $\mu\text{m}$ ) and a wall membrane content of 18% by weight.

Then, the under-listed 2 kinds of stockings were knit and dyed and, after a fixing treatment, processed with the above-described microcapsules according to the aforementioned manufacturing process.

Test article:

- ① Panty stockings.  
Leg portion: 15d/3f Kennei yarn.  
Panty and tow portions: 30d/8f woolly yarn.
- ② Panty stockings (support type).  
Leg portion: (20x13x13 DCY)x13d/3f raw silk yarn.  
Panty portion: (20x30 POY)x30d/8f woolly yarn.

Tow portion: 13d/3f raw silk yarn X 30d/8f woolly yarn X 70d/18f woolly yarn.

Binder: San Softener TAFF A (manufactured by Sanyo Chemical Industries Ltd.) ... 2% o/wf.

Buffer agent: Ultra MT (manufactured by Miteijima Kagaku Kogyo Ltd.)

After processing, drying and finish-setting were performed to provide articles and tests for resistance to washing and hand were conducted.

## Example 2

As a binder, a forced emulsified type polyurethane aqueous dispersion (Superflex E: manufactured by Daiichi Kogyo Seiyaku K.K.) was used. With regard to microcapsules, test articles and manufacturing processes, those exactly the same as Example 1 were employed.

Articles produced were tested in the same manner as Example 1.

The test results in the above 2 Examples are shown in Table 1.

Table 1

	Test Article	Microcapsules/binder add-on amount (%)	Resistance to washing	Hand
Example 1	①	1.5/1.5	5	○
	①	1.0/5.0	7	○
	②	0.8/4.0	8	△
	②	2.0/1.0	4	○
Example 2	①	1.5/1.5	4	○
	①	0.8/4.0	5	○
	②	1.0/5.0	6	△
	②	2.0/1.0	4	○
Comparative Example	①	1.0/0	1	○
	②	1.5/0	1	○

As shown in the above Table, the stockings with microcapsules adhering thereto according to the present invention have a sufficient resistance of bonding force to washing and a good hand.

#### 25 Example 3

On the outset, a seaweed extract was manufactured according to the under-described manufacturing process and further microcapsules encapsulating it were manufactured.

Twenty grams of a dry powder of the genus Laminaria belonging to the class Phaeophyceae were admixed with 120 g of JSCI purified water and then extracted at 70-80°C for 2 hours, followed by filtration to obtain 80 g of filtrate. To this filtrate, 20 g of JSCI 1,3-butylene glycol and 0.3 g of JSCI methyl paraoxybenzoate were added and heated while stirring at 70-80°C for 1 hour, followed by filtration, to obtain 100 g of seaweed extract.

Then, 3 g of the seaweed extract, 8 g of triglyceride, 9 g of squalane, 6 g of sodium sulfonated polystyrene and 4 g of urea were added to 300 g of water, pH was controlled at 4.0 and the temperature was elevated to 40°C under agitation, to emulsify. Then, 10 g of a 30% formaline aqueous solution was added and the liquid temperature was increased from 40°C to 70°C over 15 minutes while agitating at 500 rpm with a laboratory stirrer. Maintaining the temperature at 70°C for 60 minutes, a polycondensation reaction was carried out. The produced fine particles were separated from the mother liquid by a glass filter and washed with water. Then, after drying in air, heat treatment at 105°C was conducted for one minute.

The obtained microcapsules had a particle diameter of 7-15 µm (averaging 10 µm) and a wall membrane content of 18% by weight.

Then, 2 kinds of stockings, the same as those in the foregoing Example 1, were knit and dyed and, after a fixing treatment, processed with the above-described microcapsules according to the aforementioned manufacturing process.

After processing, drying and finish-setting were performed to provide articles and tests for resistance to washing and hand were conducted.

#### Example 4

As a binder, a forced emulsified type polyurethane aqueous dispersion (Superflex E: manufactured by Daiichi Kogyo Seiyaku K.K.) was used. With regard to microcapsules, test articles and manufacturing processes, those exactly the same as Example 3 were employed.

Articles produced were tested in the same manner as Example 3.

The test results in the above Examples 3 and 4 are shown in Table 2.

Table 2

	Test Article	Microcapsules/binder add-on amount (%)	Resistance to washing	Hand
Example 3	①	1.5/1.5	5	○
	①	1.0/5.0	7	○
	②	0.8/4.0	8	△
	②	2.0/1.0	4	○
Example 4	①	1.5/1.5	4	○
	①	0.8/4.0	5	○
	②	1.0/5.0	6	△
	②	2.0/1.0	4	○
Comparative Example	①	1.0/0	1	○
	②	1.5/0	1	○

As shown in the above Table, the stockings with microcapsules adhering thereto according to the present invention have a sufficient resistance of bonding force to washing and a good hand.

#### Examples 5 and 6

Two grams of clemizole sulfate, 1 g of dl-camphor, 8 g of lauryl stearate, 9 g of peppermint oil, 6 g of a sodium sulfonated polystyrene and 4 g of urea were added to 300 g of water, pH was controlled at 4.0 and the temperature was elevated to 40°C under agitation, to emulsify. Then, 10 g of a 30% formaline aqueous solution was added and the liquid temperature was increased from 40°C to 70°C over 15 minutes while agitating at 500 rpm with a laboratory stirrer. Maintaining the temperature at 70°C for 60 minutes, a polycondensation reaction was carried out. The produced fine particles were separated from the mother liquid by a glass filter and washed with water. Then, after drying in air, heat treatment at 105°C was conducted for one minute.

The obtained microcapsules had a particle diameter of 20–30 µm (averaging 24 µm) and a wall membrane content of 18% by weight (Example 5).

Microcapsules containing antipruritics were manufactured in the same manner as Example 5, except that 1.5 g of clemizole sulfate and 1.5 g of diphenhydramine were used (Example 6).

#### Example 7

Thirty grams of the microcapsules containing antipruritics in Example 5 were admixed with 30 g/t of a silicone based aqueous emulsion comprising, as a main component, an epoxy-modified dimethyl polysiloxane resin. Then, the under-listed 4 kinds of woven or knitted fabrics or cloths were applied on the reverse side thereof (as for the stockings, only on the leg portion) with the above-mentioned emulsion so that the micro-capsules might adhere in an amount of 1.5% by weight based on the weight of the fabric or the applied portion of the cloths, then dried and subjected to a heat treatment in wet at 120–130°C for one minute. The woven or knitted fabrics to which the microcapsules were thus made to adhere were dried according to a conventional method and forwarded to a finish-setting process to provide antipruritic woven or knitted fabrics.

- ① Plain weave fabric woven with No. 40 count cotton single yarn (gauze)
- ② Plain weave fabric woven with No. 30 count cotton single yarn (Yukata cloth).
- ③ Single jersey knitted with No. 40/2 count cotton plied yarn (shirting cloth).
- ④ Sock plain woven with a No. 60/2 count cotton surface yarn and a 30 denier 2 plied nylon back yarn.

Then, a bandage, Yukata and sport shirt were made up from the above woven or knitted fabrics ①, ② and ③, respectively, and tested for the resistance to washing and the hand.

Table 3

Test Article	Microcapsules/binder add-on amount (%)	Resistance to washing	Hand	Remarks
① Bandage	1.5/1.5	5	○	Invention
② Yukata	1.5/1.5	9	○	"
③ Sport shirt	1.5/1.5	12	○	"
④ Socks	1.5/1.5	11	○	"
④' Socks	0.8/4.0	20 or more	△	"
④" Socks	1.5/0	1	○	Comparative Example

## Example 8

On a polyethylene film of 14 cm X 18 cm (many air holes of a 0.5 mm diameter were bored) applied with an adhesive agent, was superimposed an antipruritic bandage of 14 cm x 18 cm applied with antipruritic microcapsules of Example 6 in the same manner as that preparing the antipruritic bandage in Example 7. Then, a release paper of 14 cm x 18 cm was laminated to manufacture an antipruritic adhesive sheet.

The antipruritic effect was evaluated by ten panelists. Then, it was found that no unpleasant feeling was felt as that would be felt when an ointment was applied and it displayed an antipruritic effect by being rubbed when one had itch.

## Examples 9 and 10

Two grams of methyl salicylate, 1 g of L-menthol, 8 g of lauryl stearate, 9 g of peppermint oil, 6 g of a sodium sulfonated polystyrene and 4 g of urea were added to 300 g of water, pH was controlled at 4.0 and the temperature was elevated to 40°C under agitation, to emulsify. Then, 10 g of a 30% formaline aqueous solution was added and the liquid temperature was increased from 40°C to 70°C over 15 minutes while agitating at 500 rpm with a laboratory stirrer. Maintaining the temperature at 70°C for 60 minutes, a polycondensation reaction was carried out. The produced fine particles were separated from the mother liquid by a glass filter and washed with water. Then, after drying in air, heat treatment at 105°C was conducted for one minute.

The obtained microcapsules had a particle diameter of 20-30 µm (averaging 24 µm) and a wall membrane content of 18% by weight (Example 9).

Microcapsules containing analgesics were manufactured in the same manner as Example 9, except that 2 g of methyl salicylate, 1 g of tocopherol acetate and 1 g of L-menthol were used (Example 10).

## Example 11

Thirty grams of the microcapsules containing analgesics in Example 9 were admixed with 30 g/l of a silicon based aqueous emulsion comprising, as a main component, an epoxy-modified dimethyl polysiloxane resin, to prepare an analgesic treating solution. Then, the under-listed 4 kinds of woven or knitted fabrics or cloths were applied on the reverse side thereof with the above-mentioned analgesic treating solution so that the microcapsules might adhere in an amount of 1.5% by weight based on the weight of the fabric or the applied portion of the cloths, then dried and subjected to a heat treatment in wet at 120-230°C for one minute. The woven or knitted fabrics to which the microcapsules containing analgesics were thus made to adhere were dried according to a conventional method and forwarded to a finish-setting process to

provide analgesic woven or knitted fabrics.

- ① Plain weave fabric woven with No. 40 count cotton single yarn (gauze).
- ② Plain weave fabric woven with No. 30 count cotton single yarn (Yukata cloth).
- ③ Single jersey knitted with No. 40/2 count cotton piled yarn (shirting cloth).
- 5      ④ Socks plain woven with a No. 60/2 count cotton surface yarn and a 30 denier 2 plied nylon back yarn.

Then, a bandage, Yukata and sport wear were made up from the above woven or knitted fabrics ①, ② and ③, respectively, and tested for the resistance to washing and the hand.

10

Table 4

Test Article	Microcapsules/ binder add-on amount (%)	Resistance to washing	Hand	Remarks
① Bandage	1.5/1.5	6	○	Invention
② Yukata	1.5/1.5	6	○	Invention
③ Sport shirt	1.5/1.5	12	○	"
④ Socks	1.5/1.5	10	○	"
④' Socks	1.5/-3	4	○	"
④" Socks	0.8/4.0	20 or more	△	"
④'" Socks	1.5/0	1	○	Comparative Example

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#### Example 12

35      On polyethylene film of 14 cm x 18 cm (many air holes of a 0.5 mm diameter were bored) applied with an adhesive, was superimposed an analgesic bandage of 14 cm x 16 cm applied with analgesic microcapsules of Example 10 in the same manner as that preparing the analgesic bandage in Example 11. Then, a release paper of 14 cm x 18 cm was laminated to manufacture an analgesic adhesive sheet.

The analgesic effect was evaluated by ten panelists. Then, it was found that no unpleasant feeling was 40 felt as that would be felt when an ointment was applied and it displayed an analgesic effect by being rubbed when one had an ache.

#### Example 13

45      A polyester based polyurethane spun-bond non-woven fabric (unit weight: 80 g/m<sup>2</sup>, and diameter of single filament: 20–30 µm) was soaked in a mixed liquid (analgesic processing liquid) comprising 30 g/t of the analgesic microcapsules of Example 10 and 30 g/t of the silicone based aqueous emulsion of Example 11, each of which adhered in an amount of 1.5% by weight.

Then, a piece of the fabric 12 cm wide and 25 cm long was cut out, both ends of which were joined 50 each other with a hot roll to fabricate an integral, analgesic supporter of a 24 cm circumference.

The analgesic effect was evaluated by 10 panelists who were tennis players and it was found that the supporter was excellent in fitability and air-permeability when it was worn, and displayed an analgesic effect by being rubbed when one felt fatigue or muscle ache.

55 Examples 14 and 15

On the supporter made of the polyurethane non-woven fabric of Example 13, the analgesic processing liquid of Example 13 was sprayed and fixed by ironing. The add-on amount of the analgesic microcapsules

was about 1.0% by weight based on the weight of the supporter (Example 14).

An analgesic processing liquid prepared by changing the amounts of both the analgesic microcapsules and silicone based resin in Example 13 to 60 g/t, was put into an aerosol can and liquified propane gas (internal pressure at 20 °C of 3.1 kg/cm<sup>2</sup>) was charged at a weight ratio of the analgesic processing liquid/the gas = 70/30. Then, in the same manner as Example 14, the supporter of the polyurethane nonwoven fabric was sprayed with the liquid and ironed (Example 15).

Both the analgesic effect and wearability were as good as Example 13. Further, as the result of the test for resistance to washing, it was found that all displayed an analgesic effect by being rubbed until washing was repeated 4-6 times.

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#### Example 16

Microcapsules containing analgesics were manufactured in the same manner as Example 9, except that 1 g of methyl salicylate and 2 g of L-menthol were used as analgesics and lauryl stearate was replaced by 15 an acrylic acid copolymer.

Then, 2 kinds of stockings, the same as the foregoing Example 1, were knitted and dyed and, after finishing a fixing treatment, a processing treatment to apply the above-mentioned analgesic microcapsules was carried out in the same manner as Example 1.

After the processing treatment, drying and finish-setting were conducted to produce articles which were 20 then tested for resistance to washing and hand.

#### Example 17

As a binder, a forced emulsified type polyurethane aqueous dispersion (Superflex E: manufactured by 25 Dai-Ichi Kogyo Seiyaku Co., Ltd.) was used. Exactly the same microcapsules, test articles and manufacturing process as Example 16 were employed.

The articles thus produced were tested in the same manner as Example 16.

The test results in the above Examples 16 and 17 were shown in Table 5.

30

Table 5

35

	Test Article	Microcapsules/binder add-on amount (%)	Resistance to washing	Hand
Example 16	①	1.5/1.5	5	○
	①	1.0/5.0	7	△
	②	0.6/3.0	7	○
	②	2.0/1.0	4	○
Example 17	①	1.5/1.5	4	○
	①	0.6/3.0	5	○
	②	1.0/5.0	6	△
	②	2.0/1.0	4	○
Comparative Example	①	1.0/0	1	○
	②	1.5/0	-	○

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As shown in Table 5, the stockings having the microcapsules of the present invention adhering thereto exhibit a sufficient resistance of adhering force to washing as well as a good hand, and further display cool and refreshing feeling and analgesic effect by being rubbed.

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#### Example 18

Fragrance processing liquids were obtained by mixing 50 parts each of aqueous dispersions of 40% microcapsules composed of a micro-envelope formed by polycondensation of methylol melamine, contain-

ing an aromatic oil of jasmine, sandalwood, rose or eucalyptus in an amount of 30%, 50% and 80%, respectively, (see Table 1, particle diameter: 5-10  $\mu\text{m}$ ) with 50 parts of an aqueous emulsion of 50% vinyl acetate. Five parts of the fragrance processing liquid were sprayed onto 95 parts of polyethylene hollow tubes for paddings, having a wall thickness of 0.3 mm, an outside diameter of 5 mm and a length of 7 mm and, after mixing lightly, the tubes were dried at 60 °C for 4 hours in a hot flue. In the course of drying, 2 hours after the commencement of drying, tubes were lightly mixed to prevent sticking to each others.

Twenty percent of the thus obtained hollow tubes having the microcapsules containing an aromatic agent adhering thereto were mixed in usual hollow tubes and stuffed in an inner net sack of a pillow case to manufacture a fragrant pillow. By 12 each of male and female panelists 30-35 years old, above 12 pillows 10 were tested for sound sleeping. The bed room was made to be in unpleasant conditions at a temperature at about 25 °C and a relative humidity of 70%.

The next morning, the following results were obtained by questionnaire:

- (1) All panelists answered that the pillows containing an aromatic agent induced sound sleeping more than the usual pillows.
- 15 (2) As for the kinds of aromatic agents, sandalwood, jasmine, rose and eucalyptus were loved in this order.
- (3) As for the content of the aromatic agents, 80% was generally preferred, except that as for eucalyptus, 30% is preferred to 80%, since some panelists were of opinion that its fragrance was too strong.

The washing test was conducted by washing the hollow tubes in steep with a neutral detergent solution 20 for 2 hours, followed by washing with water for 10 minutes. Then, the effect of fragrance emission did not substantially changed after washing. Further 10 cycles of washing operation did not substantially change the effect.

25

Table 6

Test No.	Kind of Aromatic Oil	Content of Aromatic Oil (wt.%)
1	Jasmine	30
2	Jasmine	50
3	Jasmine	80
4	Sandalwood	30
5	Sandalwood	50
6	Sandalwood	80
7	Rose	30
8	Rose	50
9	Rose	80
10	Eucalyptus	30
11	Eucalyptus	50
12	Eucalyptus	80

50

## Example 19

Forty grams per liter of microcapsules of a urea based resin containing an aromatic agent (jasmine-like fragrance, average particle diameter: 8  $\mu\text{m}$ , and wall membrane thickness: 1  $\mu\text{m}$ ) were mixed in 80 g/l of a 55 silicone based aqueous emulsion comprising an epoxy-modified dimethyl polysiloxane resin as a main ingredient. This mixed emulsion was put into an aerosol can and liquidized propane gas (internal pressure at 20 °C of 3.1 kg) was charged at a weight ratio of the mixed emulsion/the gas = 70/30. Then, the emulsion was sprayed onto the under-mentioned panty stockings and fixed by ironing (the add-on amount

of the fragrant microcapsules was made to be about 0.5% by weight based on the weight of the fabric in the adhering portion).

As the result of the test for resistance to washing, according to JIS L 0217, 103 Method, it was found that the stockings emitted fragrance by being rubbed until washing was repeated 3-6 times.

5

Panty stockings (support type).

Leg portion: (20d/1f polyurethane x 13d/3f x 13d/3f DCY) x 13d/3f raw silk yarn.

Panty portion: (20d/1f polyurethane x 30d/8f POY) x 30d/8f woolly yarn.

10

Tow portion: 13d/3f raw silk yarn x 30d/8f woolly yarn x 70d/18f woolly yarn.

#### Example 20

A mixed emulsion which was prepared by changing the content of the silicone based aqueous emulsion 15 to 40 g/t in Example 19, was sprayed upon a one-piece dress (made of georgette; polyester/rayon = 50/50) and then fixed by ironing.

As the result of the test for resistance to washing, according to JIS L 0217, 401 Method, it was found that the dress emitted fragrance by being rubbed until washing was repeated 4-7 times.

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#### Example 21

A fragrance processing agent for spray which was prepared by changing the silicone based resin in Example 19 to a hydroxypropylated starch, was sprayed upon sheeting (plain weave of 120x78/inch, with No. 45 count yarn of polyester/cotton = 35/65) and fixed by ironing.

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#### Example 22

A panty stocking was soaked in a mixed emulsion prepared by changing the contents of the microcapsules and silicone based aqueous emulsion in Example 19 to 10 g/t and 20 g/t, respectively, and 30 fixed by ironing.

The thus obtained fragrant panty stocking emitted an adequate fragrance caused by gradual breakage of microcapsules while it was worn or subjected to intentional application of friction thereto. This effect remained effective until the stocking was washed 3-6 times.

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#### [Industrial applicability]

When one wears the stockings according to the present invention, the microcapsules are broken little by little by friction while wearing, and encapsulated ascorbic acids, tocopherols or seaweed extracts are exposed and naturally contact with one's legs to provide a whitening or moisturizing effect thereto and also 40 preserve humidity of skin.

Accordingly, when going out, one can wear these stockings in such a sense as if one wore a usual whitening lotion, humidity preservative lotion or the like on one's legs before going to bed, so that the stockings can respond consumers' needs as a high value added article.

Alternatively, the textile structures of the present invention having microcapsules containing antipruritics 45 or analgesics adhering thereto, display an antipruritic effect or analgesic effect (including cool and refreshing feeling), since the microcapsules are broken little by little when the structures are used or subjected to intentional application of friction thereto. Accordingly, the effect does not vanish instantly owing to sustained emission, and has sufficient lastingness.

Further, by providing a binder to the microcapsules at an appropriate ratio, bonding force and adhesivity 50 are noticeably improved, whereby aimed add-on amount and durability of antipruritic effect or analgesic effect are acquired.

Further, the processing process requires no complicated processing steps and enables sure manufacture of the fibers or textile structures according to the present invention by applying thereto a treating agent prepared by mixing microcapsules with a binder at an appropriate ratio, followed by heat treatment.

55 Further, by providing a binder to the microcapsules at an appropriate ratio, bonding force and adhesivity are noticeably improved, whereby aimed add-on amount and resistance of effect to washing are acquired.

The processing liquid and its spray according to the present invention are applied to textile structures or the like by means of spraying or soaking, and fixed by drying with an iron or hot air dryer, so that they

are also suitable for home use.

Furthermore, regarding the paddings and pillows, since microcapsules encapsulating an aromatic agent are used, little of fragrance vanishes or is transferred to other materials during storage, so that the effect lasts long.

- 5 Since the microcapsules containing an aromatic agent are made to adhere to the paddings of the pillow, washing can be conducted with less washing cycles under milder washing conditions.

The pillows according to the present invention emit fragrance upon every movement of the head and can be used effectively.

- 10 The fragrance processing liquid and its spray according to the present invention are applied to textile structures or the like by means of spraying or soaking, and fixed by ironing, so that they are also suitable for home use. Thus, this invention has numerous advantages.

### Claims

- 15 1. A microcapsule characterized by having a particle diameter in the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and encapsulating at least a substance having a function to improve physiological conditions of human skin.
- 20 2. A microcapsule as claimed in claim 1, wherein said substance is an ascorbic acid.
3. A microcapsule as claimed in claim 1, wherein said substance is a tocopherol.
4. A microcapsule as claimed in claim 1, wherein said substance is a seaweed extract.
- 25 5. A microcapsule as claimed in claim 1, wherein said substance is an antipruritic agent.
6. A microcapsule as claimed in claim 1, wherein said substance is an analgesic agent.
7. A microcapsule as claimed in claim 1, wherein said wall membrane comprises a formaline based resin as a main component.
- 30 8. A microcapsule characterized by having a particle diameter in the range of 5-30  $\mu\text{m}$  and a wall membrane comprising a formaline based resin as a main component and encapsulating at least an aromatic agent.
- 35 9. A treating liquid characterized by containing microcapsules having a particle diameter in the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and encapsulating at least a substance having a function to improve physiological conditions of human skin, and a binder, at a weight ratio of 10:1-1:5.
- 40 10. The treating liquid claimed in claim 9, which further contains a propellant and is used as a spray.
11. A fragrance processing liquid characterized by containing microcapsules encapsulating an aromatic agent, and a binder, at a weight ratio of 10:1-1:5.
- 45 12. The fragrance processing liquid claimed in claim 11, which further contains a propellant and is used as a spray.
13. A liquid as claimed in any of claims 9 to 12, wherein said binder is a silicone based resin or urethane based resin.
- 50 14. A textile structure characterized by having microcapsules adhering thereto with a binder, said microcapsules having a particle diameter in the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and encapsulating at least a substance having a function to improve physiological conditions of human skin, said microcapsules and binder being at a weight ratio in the range of 10:1-1:5, and a total add-on amount of both the microcapsules and binder being 0.3-15% based on the weight of the fibers in a portion to which the microcapsules and binder adhere.

15. The textile structure claimed in claim 14, which is a stocking.
16. The textile structure claimed in claim 14, which is an underwear.
- 5 17. A textile sheet material characterized in that a first textile fabric having microcapsules adhering thereto with a binder is laminated with a second textile fabric or sheet, said microcapsules having a particle diameter in the range of 2-300  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and encapsulating at least a substance having a function to improve physiological conditions of human skin.

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#### Amended claims

1. (After amendment) A microcapsule for a fiber treatment agent, characterized by having a particle diameter in the range of 2-40  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and at least encapsulating at least one substance having a function to improve physiological conditions of human skin, selected from the group consisting of ascorbic acids, tocopherols, seaweed extracts, antipruritics and analgesics.
- 15 2. (Deleted).
- 20 3. (Deleted).
4. (Deleted).
- 25 5. (Deleted).
6. (Deleted).
7. A microcapsule as claimed in claim 1, wherein said wall membrane comprises a formaline based resin as a main component.
- 30 8. A microcapsule characterized by having a particle diameter in the range of 5-30  $\mu\text{m}$  and a wall membrane comprising a formaline based resin as a main component and encapsulating at least an aromatic agent.
- 35 9. (After amendment) A fiber treatment liquid characterized by containing microcapsules having a particle diameter in the range of 2-40  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and at least encapsulating at least one substance having a function to improve physiological conditions of human skin, selected from the group consisting of ascorbic acids, tocopherols, seaweed extracts, antipruritics and analgesics, and a binder, at a weight ratio of 10:1-1:5.
- 40 10. (After amendment) The fiber treatment liquid claimed in claim 9, which further contains a propellant and is used as a spray.
- 45 11. A fragrance processing liquid characterized by containing microcapsules encapsulating an aromatic agent, and a binder, at a weight ratio of 10:1-1:5.
12. The fragrance processing liquid claimed in claim 11, which further contains a propellant and is used as a spray.
- 50 13. A liquid as claimed in any of claims 9 to 12, wherein said binder is a silicone based resin or urethane based resin.
- 55 14. (After amendment) A textile structure characterized by having microcapsules adhering thereto with a binder, said microcapsules having a particle diameter in the range of 2-40  $\mu\text{m}$  and a wall membrane comprising a synthetic high molecular material and at least encapsulating at least one substance having a function to improve physiological conditions of human skin, selected from the group consisting of ascorbic acids, tocopherols, seaweed extracts, antipruritics and analgesics, said microcapsules and

- binder being at a weight ratio in the range of 10:1–1:5, and a total add-on amount of both the microcapsules and binder being 0.3–15% based on the weight of the fibers in a portion to which the microcapsules and binder adhere.
- 5    15. The textile structure claimed in claim 14, which is a stocking.
- 10    16. The textile structure claimed in claim 14, which is an underwear.
- 10    17. (After amendment) A textile sheet material characterized in that a first textile fabric having micro-  
10 capsules adhering thereto with a binder is laminated with a second textile fabric or sheet, said  
microcapsules having a particle diameter in the range of 2–40 µm and a wall membrane comprising a  
synthetic high molecular material and at least encapsulating at least one substance having a function to  
improve physiological conditions of human skin, selected from the group consisting of ascorbic acids,  
tocopherols, seaweed extracts, antipruritics and analgesics.

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## INTERNATIONAL SEARCH REPORT

International Application No PCT/JP90/00981

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>a</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl<sup>5</sup> B01J13/02, A61K7/00, 7/46, 9/50, 47/34,  
A41B11/00, D06M23/12

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>b</sup>

Classification System	Classification Symbols
IPC	B01J13/02, A61K7/00, 7/46, 9/50, 47/34, A41B11/00, D06M23/12
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>c</sup>	

Jitsuyo Shinan Koho 1946 - 1989  
Kokai Jitsuyo Shinan Koho 1971 - 1989III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>d</sup>

Category <sup>e</sup>	Citation of Document, <sup>f</sup> with indication, where appropriate, of the relevant passages <sup>g</sup>	Relevant to Claim No. <sup>h</sup>
X	JP, B2, 54-16566 (Stephen David Goldvi), 23 June 1979 (23. 06. 79), (Family: none)	1, 9, 13, 14 17
X	Asaji Kondo "Kogyo Gijutsu Library 25 Microcapsule", 20 April 1970 (20. 04. 70), Nikkan Kogyo Shinbunsha (Tokyo) p.3-11, p.19-21	1, 7, 8
X	JP, A, 47-9999 (The National Cash Register Co.), 20 May 1972 (20. 05. 72), (Family: none)	1, 9, 14, 16 17
Y	JP, U, 64-37402 (Kenmei Ureshino, Tomoko Kin), 7 March 1989 (07. 03. 89), (Family: none)	1, 5, 9, 14, 15, 16
Y	JP, A, 48-14183 (Asahi Chemical Industry Co., Ltd.), 22 February 1973 (22. 02. 73), (Family: none)	1, 9, 14, 17

<sup>e</sup> Special categories of cited documents:<sup>f</sup> "A" document defining the general state of the art which is not  
considered to be of particular relevance<sup>g</sup> "E" earlier document but published on or after the international  
filing date<sup>h</sup> "L" document which may throw doubts on priority claim(s) or  
which is cited to establish the publication date of another  
citation or other special reason not specified<sup>i</sup> "O" document referring to an oral disclosure, use, exhibition or  
other means<sup>j</sup> "P" document published prior to the international filing date but  
later than the priority date claimed<sup>k</sup> later document published after the international filing date or  
priority date and not in conflict with the application but cited to  
understand the principle or theory underlying the invention<sup>l</sup> "X" document of particular relevance; the claimed invention cannot  
be considered novel or cannot be considered to involve an  
inventive step<sup>m</sup> "Y" document of particular relevance; the claimed invention cannot  
be considered to involve an inventive step when the document  
is combined with one or more other such documents, such  
combination being obvious to a person skilled in the art<sup>n</sup> "Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search  October 18, 1990 (18. 10. 90)	Date of Mailing of this International Search Report  October 29, 1990 (29. 10. 90)
International Searching Authority  Japanese Patent Office	Signature of Authorized Officer

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, A, 49-19197 (Eurand SpA and De Felice), 20 February 1974 (20. 02. 74), & IT, A, 951409 & BE, A1, 798195 & NL, A, 7304896 & DE, A1, 2318336 & AR, A1, 198826 & BR, A0, 7302694 & FR, A1, 2254672 & GB, A, 1401143 & ES, A1, 413509 & IE, B, 37523 & FR, B3, 2254672	1, 7, 8, 11 12
Y	JP, Y1, 50-43597 (Kazuo Kamagata, Tatsuo Matsui), 12 December 1975 (12. 12. 75), (Family: none)	1, 5, 6, -14 17

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:  
 1. Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2. Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claim numbers ..... because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 5.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, Y1, 48-31968 (Nichiban Co., Ltd.), 29 September 1973 (29. 09. 73), (Family: none)	1, 3, 5, 6, 14, 17
Y	JP, A, 59-73510 (Pola Chemical Industries Inc., Matsumoto Yushi Seiyaku K.K.), 25 April 1984 (25. 04. 84), (Family: none)	1, 3
Y	JP, A, 61-224962 (Sekisui Chemical Co., Ltd.), 6 October 1986 (06. 10. 86), (Family: none)	1, 4

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE<sup>1</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.  Claim numbers ..... because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING<sup>2</sup>

This International Searching Authority found multiple inventions in this international application as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	JP, B1, 51-6733 (The Mennen Co.), 2 March 1976 (02. 03. 76), (Family: none)	9, 10, 11, 12
Y	JP, A, 58-210981 (Central Glass Co., Ltd.), 8 December 1983 (08. 12. 83), (Family: none)	9, 10
Y	JP, A, 62-12707 (Kuroda Japan K.K.), 21 January 1987 (21. 01. 87), (Family: none)	1, 2

**V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE \***

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:  
 1.  Claim numbers ..... because they relate to subject matter not required to be searched by this Authority, namely:

2.  Claim numbers ..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.  Claim numbers ....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

**VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING \***

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3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.  As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

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### (54) Fasermaterial sowie Verfahren und Behandlungsflüssigkeit zu seiner Herstellung

(57) Die Erfindung betrifft ein gefaltetes Fasermaterial, z.B. eine Papier- oder Stoffserviette, das in gefaltetem Zustand zwischen zwei Lagen (12, 14, 16, 18) des Materials eingeschlossene Mikrokapseln aufweist, die einen Duftstoff oder eine Geruch neutralisierende Sub-

stanz (26) einschließen. Das Wandmaterial der Mikrokapseln ist kraftschlüssig gegebenenfalls durch ein Bindemittel mit benachbarten Materiallagen (12, 14, 16, 18) verbunden. Beim Entfalten des Fasermaterials werden die Mikrokapseln zerstört, und ein Duft oder eine Geruch neutralisierende Substanz wird freigesetzt.

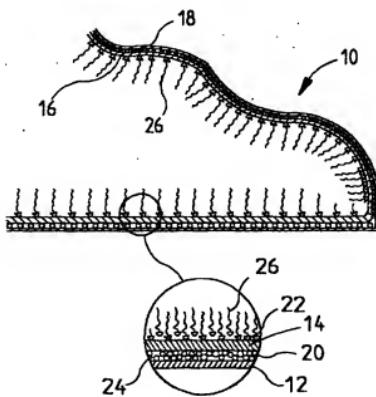


Fig. 1

## Beschreibung

[0001] Die Erfindung betrifft ein Fasermaterial gemäß dem Oberbegriff von Anspruch 1 sowie ein Verfahren zu dessen Herstellung.

[0002] Die Technik der Mikroverkapselung ist wohlbekannt. Dabei schlagen sich filmbildende Polymere auf dem einzuuhüllenden Material nieder. Die mikroskopisch kleinen Kapseln lassen sich quasi zu einem Pulver trocknen. Auf diese Weise können z.B. Lebensmittelaromen und Parfums in einer Trockenmasse umgewandelt werden, die nicht eintrocknen kann und deren Inhalt bei Bedarf durch z.B. mechanische Einwirkung freigesetzt wird.

[0003] Auch die Mikroverkapselung von Duftstoffen ist bekannt. Beispielsweise sind Parfums in Mikrokapseln eingeschlossen worden, welche dann auf einer Werbeseite für das Parfum aufgebracht werden und durch Rubbeln mit einem harten Gegenstand das Parfum freisetzen können.

[0004] Bekannt sind auch Mikrokapseln für Duftstoffe, einen Geruch neutralisierende, pflegende oder heilende Substanzen, die auf der Haut zerlieben werden und dadurch den Inhalt freigeben. Dies bringt jedoch wie bei Sprays den Nachteil mit sich, daß die Duftstoffe nicht gleichmäßig über den ganzen Körper verteilt werden. Weiter ist eine solche herkömmliche Verwendung von Mikrokapseln in anderen Gegenständen, die normalerweise keiner Reibung unterzogen werden, unbequem.

[0005] Es wäre wünschenswert, über die Mikroverkapselung so zu verfügen, daß sie bei Aufnahme der Benutzung eines Gegenstandes einen Duftstoff oder eine einen schlechten Geruch neutralisierende Substanz freisetzt, ohne daß eine gesonderte Tätigkeit für diese Freisetzung erforderlich ist.

[0006] Diese Aufgabe der Erfindung wird durch ein Fasermaterial gemäß Anspruch 1 gelöst.

[0007] Wenn das gefaltete Fasermaterial nach Anspruch 1 entfaltet wird, zerbrechen die Mikrokapseln, wobei sie einen Duftstoff, eine Geruch neutralisierende, eine pflegende oder eine hellende Substanz freisetzen.

[0008] Anspruch 2 beschreibt eine vorteilhafte Verbindung zwischen Mikrokapseln und Fasermaterial.

[0009] Anspruch 3 sorgt dafür, daß die verbrauchten Mikrokapseln durch Auswaschen aus dem Fasermaterial entfernt werden können und daß das Material erneut mit Mikrokapseln beladen werden kann.

[0010] Anspruch 4 stellt sicher, daß das Auswaschen der verbrauchten Mikrokapseln und/oder des Bindemittels mit Wasser und ggf. Tensid vorgenommen werden kann.

[0011] Gemäß Anspruch 5 erhält man eine Serviette, die beim Entfalten automatisch einen Duftstoff freisetzt. Dies ist insbesondere für festliche Essen ein schöner Auftritt.

[0012] Die Anwendung gemäß Anspruch 6 hat den Vorteil, daß zugleich mit dem Entfalten eines Bekleidungsstückes ein Duft freigegeben wird. Dies verstärkt

den Eindruck beim Benutzer, daß er ein neues sauberes Bekleidungsstück anzieht.

[0013] Die Verfahren nach Anspruch 7 bzw. 8 erlauben, ein Material auf sehr einfache Weise so zu präparieren, daß sich zwischen einzelnen Lagen des Fasermaterials Mikrokapseln befinden, die an beiden übereinandergelegten Lagen haften, so daß sie beim Auffalten des Fasermaterials aufgebrochen werden.

[0014] Bei Verwendung eines Mikrokapseln enthaltenden Fluids gemäß Anspruch 9 erhält man eine gute Bindung der Mikrokapseln zum Fasermaterial. Dadurch, daß die Duftstoff oder eine geruchneutralisierende Substanz enthaltenden Mikrokapseln in dem Bindemittel dispergiert sind, erhält man eine bleibend gleichförmige Verteilung der Mikrokapseln im Bindemittel.

[0015] Gemäß Anspruch 10 kann auch ein Endbenutzer die Ausrüstung des Fasermaterials auf einfache Weise durchführen.

[0016] Bei dem erfundungsgemäßen Fasermaterial kann es sich beispielsweise um Papier, aber auch um Stoff handeln. Das Papier bildende Fasermaterial ist gewöhnlich ein Wegwerfgegenstand, der nur einmal benutzt wird, wie beispielsweise eine Papierserviette. Bei Fasermaterial, welches einen Stoff bildet, handelt es sich gewöhnlich um wiederverwendbare Gegenstände, wie beispielsweise Stoffservietten oder Bekleidungsstücke.

[0017] Das Innere der Mikrokapseln besteht gewöhnlich aus einer Flüssigkeit die einen Duftstoff freigibt oder eine geruchneutralisierende Wirkung aufweist. Es kann sich aber auch um ein Festkörpermaterial handeln, das adsorbiert eine Flüssigkeit oder ein Gas aufweist, das duftet oder einen Geruch neutralisiert, oder direkt verdampft (Sublimation). Der Kapselinhalt kann auch eine pflegende oder hellende Wirkung haben. In den Kapseln können auch Mischungen aus den vorgenannten Substanzen enthalten sein, oder die Mikrokapseln können ein Gemisch aus Mikrokapseln mit jeweils einem einzigen Inhaltsstoff sein.

[0018] Durch Zerbrechen der Mikrokapseln wird deren Inhalt freigesetzt.

[0019] Die Wand der Mikrokapseln kann aus unterschiedlichen einerseits mit dem Fasermaterial direkt oder über ein Bindemittel verbindbaren andererseits bei mechanischer Belastung brechenden Materialien ausgewählt sein, wie z.B. Silikonelastomeren, Polyurethenen, Nitrigummimären, Chloropregnummimären, Polyvinylalkoholen, Silikonen, Äthylen/Vinylact-Polymeren, Acrylharzen und Hamstoff-Aldehyd-Polymer. Die Mikrokapseln können gemäß dem Verfahren von Beispiel 10 der US 3 516 941 A hergestellt werden.

[0020] Die Größen der Mikrokapseln betragen im allgemeinen etwa 2 - 300 µm, vorzugsweise etwa 4 - 80 µm und insbesondere etwa 15 - 25 µm. Durch die gewählte Mikrokapselgröße kann gesteuert werden, wie schwer bzw. leicht die Kapseln zerbrechen, wenn die beiden Fasermateriallagen, mit denen sie verbunden

sind, auseinandergezogen werden.

[0021] Falls ein Bindemittel verwendet wird, um die Mikrokapseln mit den Faserlagen zu verbinden, kann dieses aus einer großen Vielfalt von Bindemitteln ausgewählt werden, wie Polyurethanen, Polyacrylaten, Polyvinylharzen (z. B. Polyvinylalkohol, Polyvinylchlorid), Polyamiden, Polyester, Polyolefinen, Stärken, Gummiarabicum, Gelatine, Cellulose und Silikonkautschuk. Für eine Anwendung bei textilen Materialien werden aus diesen Bindemitteln diejenigen bevorzugt, die in Wasser und ggf. Tensid löslich oder dispergierbar sind.

[0022] Insgesamt werden die beschriebenen Materialien so ausgewählt, daß der Eigenzusammenhalt der Mikrokapseln schwächer ist als die Haftung derselben an dem Fasermaterial bzw. dem Bindemittel und daß die Haftung des Bindemittels an dem Fasermaterial stärker ist als der Eigenzusammenhalt des Bindemittels.

[0023] Die Erfindung wird nachstehend unter Bezugnahme auf die Zeichnung anhand von Ausführungsbeispielen genauer erläutert. In der Zeichnung zeigen:

Figur 1: einen Schnitt durch einen Teil eines vierlagigen Materials, bei dem zwischen den einzelnen Materiallagen Verbundschichten aus einem Bindemittel und Mikrokapseln, die einen Duftstoff enthalten, liegen, gezeigt in teilweise aufgefaltetem Zustand;

Figur 2: einen Schnitt durch ein zweilagiges Material, bei welchem Mikrokapseln zwischen mit den Materiallagen verbundenen Bindemittelschichten liegen; und

Figur 3: eine Sprayflasche, die eine Dispersion aus Mikrokugeln und Bindemittel enthält und zum Herstellen von Bindemittel/Mikrokapsel-Verbundschichten auf Fasermaterialien dient.

[0024] Figur 1 zeigt vier Lagen eines Fasermaterials, wobei jeweils zwei Lagen, nämlich die Lagen 12 und 14 und die Lagen 16 und 18, übereinander gefaltet sind. Zwischen den Lagen 12 und 14 bzw. 16 und 18 befinden sich Mikrokapseln 20, die kraftschlüssig mit beiden jeweils übereinanderliegenden Lagen verbunden sind.

[0025] Die Verbindung zwischen den Mikrokapseln und die Verbindung von Mikrokapseln mit dem Fasermaterial erfolgt bevorzugt durch ein Bindemittel 24. Die Mikrokapseln zwischen den Lagen 14 und 16 lagen ursprünglich ebenfalls in unverkehrtem Zustand an beiden Lagen haftend vor. Durch Trennung der Lagen 14 und 16 sind die Mikrokapseln beschädigt worden, wodurch ihr Inhalt, ein Duftstoff oder eine Geruch neutralisierende Substanz freigesetzt worden ist wie durch gewellte Linien 26 angedeutet.

[0026] Bei dem oben beschriebenen Fasermaterial, welches z.B. eine zusammengefaltete Serviette darstel-

len kann, werden die in den Mikrokapseln 20 enthaltenen Duftstoffe, geruchsneutralisierenden, pflegenden oder heilenden Substanzen so lange zusammengehalten, bis die Faserlagen aufgefaltet werden. Dann wird flächig der Inhalt der Kapseln freigesetzt.

[0027] Bei den Faserlagen kann es sich auch um übereinandergelegte Lagen eines Kleidungsstückes handeln. So kann man z.B. nach dem Waschen Taschentücher kurz bevor man sie zusammenfaltet mit einer Flüssigkeit besprühen, die ein Bindemittel und hierin verteilt Duftstoff enthaltende Mikrokapseln aufweist. Das Bindemittel kann z.B. Reisstärke sein. Dieses Bindemittel wird beim nächsten Waschen des Taschentuches mit den Resten von Mikrokapseln herausgewaschen. Faltet man das Taschentuch nach dem Besprühen zusammen, so sind die Mikrokapseln über die getrocknete Reisstärke nun mit zwei übereinanderliegenden Lagen des Taschentuches verbunden. Bei Auffalten des Taschentuches werden die Mikrokapseln mechanisch zerstört, da ihr Kapselmaterial so gewählt ist, daß die mechanische Festigkeit der Mikrokapseln kleiner ist als die Stärke der Verbindung zwischen Mikrokapsel-Wandmaterial und dem Stoff des Taschentuches über die dazwischenliegende Reisstärke-Bindemittelschicht.

[0028] Ähnlich kann man auch andere Wäschestücke oder Kleidungsstücke mit einer Mikrokapseln enthaltenen Flüssigkeit besprühen, vorzugsweise durch Betätigen eines Sprays. Der beim Auffalten entstehende Duft gibt dem Benutzer ein verstärktes Gefühl dafür, daß das

Wäsche- oder Bekleidungsstück, das er gerade in Benutzung nimmt, frisch gewaschen ist.

[0029] Bei dem abgewandelten Ausführungsbeispiel nach Figur 2 sind die Mikrokapseln 20 zwischen zwei Bindemittelschichten 24a, 24b eingeschlossen, die von der Lage 12 bzw. der Lage 14 getragen sind. Die Bindemittelschicht 24a und 24b waren zunächst eine durchgehende Bindemittelschicht, die auf eine durchgehende Materiallage aufgebracht (z.B. aufgesprührt) wurde, bevor die Lagen 12, 14 übereinandergelegt wurden.

[0030] Auf diese ursprünglich einzige durchgehende Bindemittelschicht wurden bei ebenfalls noch nicht zusammengefalteten Lagen 12, 14 die Mikrokugeln 20 aufgebracht, z.B. aufgestäubt oder aufgeslebt.

[0031] Die ursprünglich durchgehende Lage mit der ursprünglich durchgehenden Bindemittelschicht und der darüber liegenden Schicht aus Mikrokapseln wurde dann gefaltet, wodurch die Mikrokapseln nun über die beiden Bindemittelschichten 24a, 24b mit den Lagen 12, 14 verbunden sind.

[0032] Zieht man die beiden Lagen 12, 14 auseinander, so stellt die nun innere Mikrokapselschicht eine Spaltfläche dar, und die Bindemittelschicht 24a und 24b trennen sich unter Zerstörung der Mikrokapseln 20. Damit wird ein Duftstoff oder eine geruchsneutralisierende Substanz freigegeben, die sich im Inneren der Mikrokapseln 20 befindet.

[0033] Bei dem in den Mikrokapseln eingeschlossenen Duftstoff oder geruchsneutralisierenden Material

kann es sich auch um ein Festkörpermaterial handeln, welches nach der Zerstörung der Mikrokapselwand sublimiert.

[0033] Es versteht sich, daß man die übereinanderliegenden Lagen aus Fasermaterial über die gesamte Fläche hinweg mit Bindemittel und Mikrokapseln beschichten kann oder auch nur über Teilbereiche ihrer Kontaktfläche. Auf diese Weise kann man die Kraft, die notwendig ist, um die Lagen aufzufalten und die Intensität des beim Auffalten entstehenden Duftes regulieren.

[0034] Handelt es sich bei dem Fasermaterial um ein textiles Material, so wird vorzugsweise ein Bindemittel verwendet, das beim Waschen des textilen Materials in Lösung geht. Auf diese Weise löst sich dann die an den Lagen noch hängenden Reste der Mikrokapselwände beim Waschen des textilen Materials ab.

[0035] Falls gewünscht, kann man zusätzlich auch das Material der Mikrokapseln selbst so wählen, daß es beim Waschen in Lösung geht.

[0036] Für manche Anwendungsfälle reicht es auch aus, die Mikrokapseln unmittelbar nach ihrer Herstellung, wenn die Kapselwände noch klebrig sind, einfach auf die Oberfläche des Fasermaterials zu stäuben, bevor die Lagen des Fasermaterials übereinandergefasst werden.

[0037] Bei Wäsche- oder Kleidungsstücken, die oft wieder verwendet werden, kann man dem Benutzer eine Ausrüst-Flüssigkeit zur Verfügung stellen, mit welcher er selbst Bindemittel-Mikrokapsel-Verbundschichten erzeugen kann, wie sie obenstehend unter Bezugnahme auf die Figuren 1 und 2 erläutert wurden.

[0038] Gemäß Figur 3 enthält eine Sprayflasche 28 eine wässrige Lösung aus einem Bindemittel (etwa Reisstärke) und Mikrokapseln 20. Die Sprayflasche 28 kann durch ein Treibgas unter Druck gesetzt sein oder einen Pumpmechanismus aufweisen, wie bei Sprayflaschen üblich.

#### Patentansprüche

1. Gefaltetes Fasermaterial, dadurch gekennzeichnet, daß es in gefaltetem Zustand zwischen mindestens zwei Lagen des Materials verschlossene Mikrokapseln (20) aufweist, die einen Duftstoff, eine geruchsneutralisierende, eine heilende, eine pflegende Substanz (23) oder Mischungen dieser Substanzen einschließen und deren Wandmaterial kraftschlüssig mit den benachbarten Materiallagen (12, 14; 16, 18) verbunden ist.
2. Fasermaterial nach Anspruch 1, dadurch gekennzeichnet, daß die Mikrokapseln (20) durch ein Bindemittel (24) mit den benachbarten Materiallagen (12, 14; 16, 18) verbunden sind.
3. Fasermaterial nach Anspruch 1 oder 2, dadurch

gekennzeichnet, daß die Mikrokapseln (20, 22) auswaschbar sind.

4. Fasermaterial nach Anspruch 3, dadurch gekennzeichnet, daß das Wandmaterial der Mikrokapseln und/oder ein Bindemittel (24), durch welches die Mikrokapseln (20) mit dem Fasermaterial verbunden sind, in Wasser, zumindest in Waschmittel enthaltendem Wasser, löslich oder dispergierbar ist.
5. Fasermaterial nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß es eine Serviette aus Papier oder Stoff bildet.
- 15 6. Fasermaterial nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß es ein Wäsch- oder Bekleidungsstück oder einen Teil eines solchen bildet.
- 20 7. Verfahren zur Herstellung eines Fasermaterials nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß man (a) ein Fasermaterial im ungefalteten Zustand mit einem Mikrokapseln enthaltenden Fluid besprüht, (b) das Fasermaterial anschließend sofort so unter Anwendung von leichtem Druck faltet, daß zumindest ein Teil der Mikrokapseln an beiden so übereinander gelegten Lagen haften, (c) gegebenenfalls vorhandene Flüssigkeit verdunsten läßt.
- 25 8. Verfahren zur Herstellung eines Fasermaterials nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß man (a) ein Fasermaterial in ungefaltetem Zustand mit einer Bindemittelschicht (24a, 24b) versieht, (b) auf das Bindemittel einen Duftstoff oder eine geruchsneutralisierende Substanz enthaltende Mikrokapseln (20) aufbringt und (c) das Fasermaterial unter Anwendung von leichtem Druck faltet, so daß zumindest ein Teil der Mikrokapseln an beiden übereinandergelegten Bindemittelschichten haftet.
- 40 9. Behandlungsflüssigkeit zur Verwendung in Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß sie ein auf dem Fasermaterial haftend anbringbares Bindemittel umfaßt, in welchem Duftstoffe oder eine geruchsneutralisierende Substanz enthaltende Mikrokapseln dispergiert sind.
- 45 10. Behandlungsflüssigkeit zur Verwendung in Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß sie zusammen mit einem sich mit ihr nicht vermischenden Treibgas in einem Behälter eingeschlossen ist.
- 55

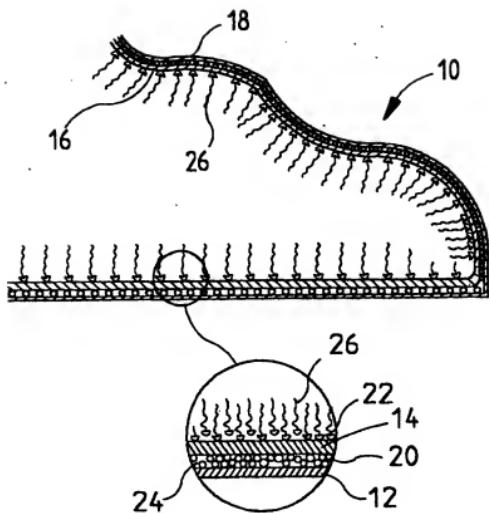


Fig. 1

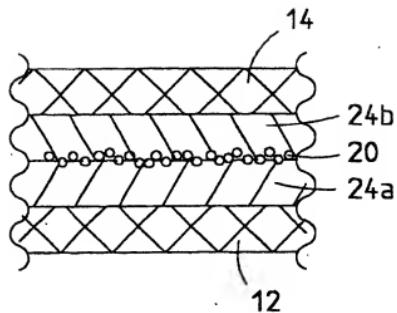


Fig. 2

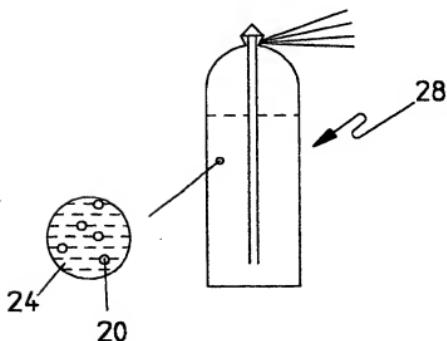


Fig. 3

# UK Patent Application GB 2 140 820 A

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## (54) Perfume-containing carrier having surface-modified particles for detergent composition

(57) A perfume-containing carrier is provided for use in admixture with a particulate laundry detergent composition or as an additive to the wash solution separate from the detergent composition to impart a pleasing fragrance to laundered fabrics. The perfume-containing carrier comprises (i) discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume, the said perfume being adsorbed or absorbed or adsorbed and absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound i.e. a primary, secondary or tertiary amines or their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the fabric-adhesive agent being in contact with the particles and forming at least a partial coating on the surface, the perfume-containing carrier containing less than 5%, of surface active detergent compounds other than cationics.

GB 2 140 820 A

**SPECIFICATION****Perfume-containing carrier having surface-modified particles for laundry composition**

- 5 The present invention relates to perfume-containing carriers which significantly enhance the substantivity of perfume to laundered fabrics. More particularly, this invention relates to particulate detergent compositions which include as a component thereof a perfume-containing carrier which is able to impart a pleasing perfume fragrance to the finished laundered fabrics with only minimal amounts of perfume. 5
- 10 The present application is related to copending U.S. Application Serial No. 499,926 filed on 1st June, 1983, which corresponds to G.B. Application No. which claims priority therefrom under the International Convention, which describes a perfume-containing carrier comprising discrete particles containing a clay mineral (other than talc) and/or a zeolite; and a perfume. 10
- 15 Perfume substances which modify or enhance the aroma of detergent compositions or impart a pleasing aroma thereto are well-known in the art. U.S. Patent No. 4,131,555 and 4,228,026, are illustrative of patents which describe substances intended to impart a pleasing aroma or fragrance to liquid and granular detergent compositions. The described methods of preparation consist of mixing the perfume substances, in solid form, with the prepared detergent 15
- 20 compositions to form a homogeneous composition. Perfumes which are in liquid form are conventionally added to liquid detergent compositions as a component thereof or sprayed upon the surface of granular detergent compositions. However, detergent compositions which are thus prepared are unable to impart a perfume fragrance to the fabrics being laundered notwithstanding the enhanced aroma of the composition itself. Primarily, this is because the perfume 20
- 25 substances in the detergent composition are rapidly dispersed and diluted during laundering in the aqueous wash solution along with the water-soluble components of the detergent composition. Consequently, only a relatively minor amount of the perfume is available to contact and adhere to the fabric being laundered, the major portion of the perfume being drained from the washing machine with the wash solution during the wash cycle. Moreover, to the extent that some perfume is still in contact with the fabric after the washing operation, it tends to be 25
- 30 dissipated subsequently during drying, such as, for example, in a gas or electric dryer in which the washed fabrics are tumbled at relatively high temperatures. As a result, fabrics laundered with conventional detergent compositions generally retain only a very faint perfume fragrance which has no particular aesthetic appeal to the user. There is, therefore, a need in the art for an additive to conventional detergent compositions which can effectively provide a perfume fragrance to fabrics being laundered such that the finished laundered fabrics have added appeal to the user. 30
- 35 U.S. Patent No. 4,259,373 discloses a fabric conditioning article for use in an automatic washer or dryer consisting of a sealed water-insoluble pouch containing what is described as a softener/antistat composition. In Example II of that specification, there is described a preparation procedure for such antistat composition wherein clay and solid perfume are mixed and the mixture then blended with sprayed particles of certain quaternary ammonium salts. The resulting composition is then filled into a sealed polyester pouch. 35
- Included among the perfume-containing carriers of the invention described is a particular embodiment which comprises a perfume, particles of clay and a quaternary ammonium compound (sometimes referred to herein as a "QA" compound for convenience). Compositions containing clay and QA compounds are broadly described in the art relating to fabric softeners and anti-stat compositions. U.S. Patent No. 3,886,075, for example, describes a composition containing a smectite clay, a water-soluble QA compound and an "amino compatibilizing agent" which is said to provide fabric softening and anti-static effects. U.S. Published Patent Application No. B305,417 describes a granular laundering composition comprising a soap-based granule, a smectite-type clay and a quaternary ammonium antistatic agent. In U.S. Patent No. 3,862,058, a clay and a quaternary ammonium compound are added to a non-soap synthetic detergent compound to provide a granular laundry detergent composition. U.S. 45
- 50 Patent Nos. 3,993,573 and 3,954,632 describe fabric softening compositions containing the aforementioned clay and QA compounds in combination with a so-called "acid compatibilizing agent". U.S. Patent No. 4,292,035 discloses a softening composition comprising smectite clay; an amine or quaternary ammonium compound as a softening agent; and an anionic surfactant wherein the fabric softening agent is reacted with the clay to form an "organo-clay complex" 50
- 55 60 prior to the addition of the anionic surfactant.
- The methods described in the art for preparing the aforementioned fabric softening compositions are characterised by either a deposition of QA compound upon granules composed of a uniform blend of clay with detergent and other ingredients (rather than a preferential deposition upon clay granules) or alternatively, the QA compound is reacted with the clay to provide a modified clay in which preferably from about 10 to about 60 molar percent of the exchangeable 60
- 65 65

cations are alkyl substituted ammonium ions. Thus, for example, U.S. Patent Nos. 3,862,058 and 3,886,075 describe a method of preparation whereby the clay is initially admixed in a crutcher with the detergent, builder and other ingredients of the laundering compositions and the resulting mixture then spray-dried to form granules. The QA compound is thereafter sprayed upon the granules from a melt, it being a critical aspect of the method of preparation to avoid spraying the detergent granules with an aqueous solution or suspension of the QA compound. United States Published Patent Application B305,417 discloses a method of preparation wherein clay is mixed with soap-based granules in a drum mixer. The QA compound is then added to the resulting composition by spraying from a melt. U.S. Patent No. 3,594,212 describes a method of softening fibrous materials wherein such materials are successively impregnated with an aqueous dispersion of clay and an aqueous solution of QA compound, the amount of QA compound in solution being sufficient to effect at least a partial cation exchange with the clay retained on the fibrous material. In U.S. Patent No. 3,948,790 to Speakman, there is described a procedure for preparing "quaternary ammonium clays" whereby a QA compound is reacted with clay by slurring the untreated clay in a solution containing the desired quantity of QA compound. The QA compounds which may be thus employed are said to be restricted to short-chain compounds having a maximum of four carbon atoms per chain, the total number of carbon atoms in the compound not exceeding eight. The quantity of such QA compound added to the solution is controlled so as to provide the desired degree of ion exchange with the clay. The examples of the patent describe various treated clays in which from about 5 to 40% of the exchangeable cations are replaced by quaternary ammonium cations, the amount of QA compound in solution being necessarily restricted to that which is required to effect a partial exchange reaction with the clay. Accordingly, the prior art does not contemplate the particular combination of clay particle and QA compound employed in the present invention, much less contemplate using such combination as a carrier for perfume in accordance with the present invention.

The present invention provides an improved perfume-containing carrier comprising: (i) discrete particles containing at least 75%, by weight, of a clay mineral (other than talc) and/or a zeolite; (ii) a perfume, the said perfume being adsorbed and/or absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammnonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of detergent compounds other than cationic detergents.

In accordance with process aspect of the invention, the deposition of perfume on laundered fabrics is effected by contacting the stained and/or soiled materials to be laundered with an aqueous solution or dispersion which contains the above-defined perfume-containing carriers. The term "perfume" as used herein refers to odouriferous materials which are able to provide a pleasing fragrance to fabrics, and encompasses conventional materials commonly used in detergent compositions to counteract a malodour, in such compositions and/or provide a pleasing fragrance thereto. The perfumes are preferably in the liquid state at ambient temperature, although solid perfumes are also useful. Included among the perfumes contemplated for use herein are materials such as aldehydes, ketones, esters and the like which are conventionally employed to impart a pleasing fragrance to liquid and granular detergent compositions. Naturally occurring plant and animal oils are also commonly used as components of perfumes. Accordingly, the perfumes useful for the present invention may have relatively simple compositions or may comprise complex mixtures of natural and synthetic chemical components, all of which are intended to provide a pleasant odour or fragrance when applied to fabrics. The perfumes used in detergent compositions are generally selected to meet normal requirements of odour, stability, price and commercial availability. A description of the materials conventionally used in detergent perfumery is set forth by R. T. Steltenkamp, *The Journal of the American Oil Chemists Society*, Vol. 45, No. 6, pp. 429-432, such disclosure being incorporated herein by reference.

The term "particles" as used throughout the specification and claims with regard to the perfume-containing carrier is intended to encompass a wide variety of particulate matter of differing shape, chemical composition, particle size and physical characteristics, the essential common characteristic being that such particles contain at least 75%, by weight, of a clay mineral or a zeolite or a mixture thereof. The particles are desirably free-flowing in nature. The "weight percent" of the clay mineral and the zeolite refers to the weight of such materials including the water and impurities associated with the particular clay or zeolite employed. Accordingly, the carrier particles may be in the form of finely divided powders, as well as relatively larger-sized granules beads or agglomerated particles, and may be produced by diverse methods of manufacture such as spray-drying, dry-blending or agglomeration of individual

- components. Particularly preferred carrier particles for use herein are bentonite agglomerates produced by the method described in USSN 366,587, filed 8th April, 1982, which corresponds to G.B. Application No. 83.09605 (published as 2121843A), the disclosure of which is incorporated herein by reference. The carrier particles may thus optionally include in addition to 5 the clay mineral and/or zeolite, materials which are compatible with conventional laundering compositions, examples of suitable materials including binding or agglomerating agents, e.g. sodium silicate, dispersing agents, detergent builder salts, filler salts as well as common minor ingredients present in conventional laundry detergent compositions such as dyes, optical brighteners, anti-redeposition agents and the like. For the purposes of the present invention, the 10 particles should contain less than about 5%, by weight, of surface active detergent compounds, preferably less than about 3%, by weight, and most preferably are substantially free of surfactants.
- The term "discrete" as used herein with regard to the particles refers to the fact that such particles are employed in the present invention as individually distinct particles, thus excluding, 15 for example, carrier particles which are encompassed within a matrix of other materials, or which are blended with other ingredients such that the particles become a component of a larger aggregate material rather than being in the form of individual and distinct particles.
- The present invention is characterised by an effective perfume-containing carrier wherein the carrier particles contain at least 75%, by weight, preferably at least 90%, by weight, of a clay 20 mineral other than talc and/or a zeolite. The major portion of the perfume associated with the carrier, preferably at least 95% thereof, is adsorbed and/or absorbed on the said particles, the terms "adsorbed" and "absorbed" being used herein to refer to the physical association of the perfume with the carrier particles. Unlike conventional practice wherein the perfumes added to granular detergent compositions are sprayed upon or otherwise contacted with the water-soluble 25 spray-dried granular powders, the perfumes employed in the present invention are contacted with particles of a clay mineral or zeolite which are, for the most part, water-insoluble. It has been found that the perfume thus associated with the carrier particles remains primarily concentrated upon such particles during laundering rather than being dispersed in the aqueous wash solution. This provides a significant advantage during laundering insofar as the perfume- 30 containing carrier particles in the wash solution are likely to contact the laundered fabrics and be dispersed thereupon, particularly in a washing machine where the wash solution is mechanically drained through the fabric during the wash cycle. The perfume is thus maintained proximate to the finished laundered fabric, preventing the dissipation of the perfume fragrance from such fabrics.
- 35 Moreover, retention of the carrier particles upon the surface of the laundered fabrics is enhanced by the fabric adhesive agent which forms at least a partial coating upon the surface of the particles. Thus, for example, the use of an anionic or nonionic surfactant as a fabric adhesive agent in accordance with the present invention provides a pasty adhesive-like surface to the carrier particles, increasing the likelihood of such particles being entrapped upon the 40 fabrics during laundering. The use of a cationic compound similarly enhances fabric adhesion, albeit in a different manner. Although applicants do not wish to be bound by a particular theory of operation, it is believed that the deposition of a cationic compound upon the surface of the particles imparts a positive surface charge to such particles which creates a driving force for the positively charged particles to attach themselves to the negatively charged surface of the fabrics 45 being laundered, and particularly, to fabrics containing substantial amounts of cotton. Furthermore, the surface modified particles of clay or zeolite are generally hydrophobic in nature, the clay itself being hydrophilic. The hydrophobicity of the particles is particularly advantageous in hand-wash laundering operations because the hydrophobic particles are not as readily dispersible in the aqueous hand-wash solution as untreated particles and, therefore, tend to remain 50 upon the surface of the wash solution for longer periods of time. This has the effect of enhancing the availability of such particles for contact with and deposition upon the fabrics being laundered, thereby increasing the likelihood of maintaining the desired perfume fragrance in the hand-washed fabrics.
- The perfume-containing carriers of the present invention are comprised of three essential 55 ingredients: a clay mineral and/or a zeolite, a perfume; and a defined fabric-adhesive agent. The weight ratio of clay mineral or zeolite to perfume in the carriers is generally from about 10:1 to about 200:1 and preferably from about 20:1 to about 100:1. The weight of perfume in the carrier will generally vary within the range of from about 0.2 to 10%, and preferably from about 0.5 to 5%, by weight, thereof. The carriers may be conveniently employed during home 60 laundering as additives to a laundry washing bath separate from the detergent composition, such as, for example, a rinse-cycle additive or alternatively, the carriers may be incorporated into a conventional laundry detergent composition as a component thereof. Such fully-formulated detergent compositions generally comprise (a) from about 0.1 to about 50%, by weight, preferably from about 5 to about 30%, by weight, of the said perfume-containing carrier; and (b) from about 2 to about 50%, by weight preferably from about 5 to about 40%, by weight.

and most preferably from about 5 to about 30%, by weight, of a surface active agent selected from the group consisting of anionic, nonionic, cationic, ampholytic and zwitterionic detergents, the amount of such detergents being additional to any detergent compound in the perfume-containing carrier. The detergent compositions optionally also contain from 0 to about 70%, by weight, of a detergent builder salt, a concentration of from about 5 to about 50% being particularly preferred. The balance of the composition will predominantly comprise water, filler salts, such as, sodium sulphate, and optionally minor components such as binders, optical brighteners, pigments, dyes and the like which are conventional adjunct materials in detergent formulations.

For purposes of economy it is preferred that the major portion, and in most instances, preferably substantially all, of the perfume contained in the detergent composition be provided by the carriers. However, the detergent compositions useful herein may also include perfumes additional to that employed in conjunction with the above-described carriers to provide a pleasant odour to the wash solution or to the composition itself. The use of additional perfumes may also be advantageous in instances where it is used in conjunction with a limited amount of a more expensive perfume. Thus, for example, it may be economically desirable to utilize a minor amount of a relatively expensive perfume with the carrier of the invention and provide relatively larger amounts of a less expensive perfume to the granular detergent composition as a supplementary fragrance, the latter perfume being added by techniques known in the art, such as, by spraying the granular detergent powder.

The clay minerals which are generally useful herein include a wide variety of materials included among which are smectite-type clays; kaolinite, metakaolin; and attapulgite. Of the above-mentioned types of clay minerals, the smectite-type clays are preferred because they advantageously provide desirable softening effects to the laundered fabrics in addition to serving as a carrier for perfume in accordance with the present invention. A detailed description of the various types of clay minerals, all of which may be used in the present invention, is set forth by B.K.G. Theng, *The Chemistry of Clay Organic Reactions*, John Wiley & Sons, (1974) pp. 1-15, such disclosure being incorporated herein by reference.

The crystalline types of zeolite which may be employed herein include those described in "Zeolite Molecular Sieves" by Donald W. Breck, published in 1974 by John Wiley & Sons, typical commercially available zeolites being listed in Table 9.6 at pages 747-749 of the text, such table being incorporated herein by reference. Zeolite structures of type A are especially desirable and are extensively described in the art; see, for example, page 133 of the aforementioned Breck text as well as U.S. Patent No. 2,882,243. Type 4A zeolite is advantageously employed, the univalent cation of such zeolite being sodium and the pore size of the zeolite being about 4 Angstroms.

The aforementioned smectite-type clays are three-layer clays characterised by the ability of the layered structure to increase its volume several-fold by swelling or expanding when in the presence of water to form a thixotropic gelatinous substance. There are two classes of smectite-type clays: in the first class, aluminium oxide is present in the silicate crystal lattice; in the second class, magnesium oxide is present in the silicate crystal lattice. Atom substitution by iron, magnesium, sodium, potassium, calcium and the like can occur within the crystal lattice of the smectite clays. It is customary to distinguish between clays on the basis of their predominant cation. For example, a sodium clay is one in which the cation is predominantly sodium. With regard to the present carriers, aluminium silicates wherein sodium is the predominant cation are preferred, such as, for example, bentonite clays. Among the bentonite clays, those from Wyoming (generally referred to as western or Wyoming bentonite) are especially preferred.

Preferred swelling bentonites are sold under the trademark Mineral Colloid, as industrial bentonites, by Benton Clay Company, an affiliate of Georgia Kaolin Co. These materials which are the same as those formerly sold under the trademark THIXO-JEL, are selectively mined and beneficiated bentonites, and those considered to be most useful are available as Mineral Colloid No's 101, etc. corresponding to THIXO-JEL's No's. 1, 2, 3 and 4. Such materials have pH's (6% concentration in water) in the range of 8 to 9.4, maximum free moisture contents of about 8% and specific gravities of about 2.6, and for the pulverized grade at least about 85% (and preferably 100%) passes through a 200 mesh U.S. Sieve Series sieve (which has openings 74 microns across). More preferable, the bentonite is one wherein essentially all the particles (i.e. at least 90% thereof, preferably over 95%) pass through a No. 325 siava (U.S. Sieve Series) (which has openings 44 microns across) and most preferably all the particles pass through such a siava. The swelling capacity of the bentonites in water is usually in the range of 3 to 15 ml./gram, and its viscosity, at a 6% concentration in water, is usually from about 8 to 30 centipoises.

In a particularly preferred embodiment of the invention, the carrier particles comprise agglomerates of finely divided bentonite, of particle sizes less than No. 200 sieve, agglomerated to particles of sizes essentially in the No's. 10-100 sieve range (U.S. Sieve series) (which have openings 2000 to 149 microns across), of a bulk density in the range of 0.7 to 0.9 g./ml and a

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moisture content of 8 to 13%. Such agglomerates include about 1 to 5% of a binder or agglomerating agent to assist in maintaining the integrity of the agglomerates until they are added to water, in which it is intended that they disintegrate and disperse. A detailed description of the method of preparation of such agglomerates is set forth in the aforementioned 5 U.S. Serial No. 366,587, filed 8th April, 1982 which corresponds to G.B. Application No. 83.09605 (published as 2121843A) which is incorporated herein by reference.

Instead of utilizing the THIXO-JEL or Mineral Colloid bentonites one may employ products, such as that sold by American Colloid Company, Industrial Division, as General Purpose Bentonite Powder, 325 mesh, which has a minimum of 95% thereof finer than 325 mesh or 44 10 microns diameter (wet particle size) and a minimum of 96% finer than 200 mesh or 74 microns diameter (dry particle size). Such a hydrous aluminium silicate is comprised principally of montmorillonite (90% minimum), with smaller proportions of feldspar, biotite and selenite. A typical analysis, on an "anhydrous" basis, is 63.0% silica, 21.5% alumina, 3.3% of ferric iron (as  $\text{Fe}_2\text{O}_3$ ), 0.4% of ferrous iron (as FeO), 2.7% of magnesium (as MgO), 2.6% of sodium and 15 potassium (as  $\text{Na}_2\text{O}$ ), 0.7% of calcium (as CaO), 5.6% of crystal water (as  $\text{H}_2\text{O}$ ) and 0.7% of trace elements.

Although the western bentonites are preferred it is also possible to utilize other bentonites, such as those which may be made by treating Italian or similar bentonites containing relatively small proportions of exchangeable monovalent metals (sodium and potassium) with alkaline 20 materials, such as sodium carbonate, to increase the cation exchange capacities of such products. It is considered that the  $\text{Na}_2\text{O}$  content of the bentonite should be at least about 0.5%, preferably at least 1% and more preferably at least 2% so that the clay will be satisfactorily swelling, with good softening and dispersing properties in aqueous suspension. Preferred 25 swelling bentonites of the types described above are sold under the trade names Laviosa and Winkelmann, e.g. Laviosa AGB and Winkelmann G-13.

The silicate, which may be employed as a binder to hold together the finely divided bentonite particles in agglomerated form, is preferably a sodium silicate of  $\text{Na}_2\text{O}:\text{SiO}_2$ , e.g. 1:2.4. The silicate is water soluble and solutions thereof at concentrations up to about 50%, by weight, may be employed in the preparation of the aforementioned bentonite agglomerates, all of such 30 solutions being free flowing, especially at the elevated temperatures to which the silicate solution is preferably heated during the preparation procedure.

The cationic compounds are employed as fabric adhesive agents in the carriers of the present invention in an amount of from about 0.2 to about 16%, and preferably from about 1 to 5%, by weight. In the fully-formulated detergent compositions of the present invention, the cationic 35 compounds are present in an amount of from about 0.01 to about 10%, more usually from about 0.05 to 2%, and preferably from about 0.1 to 1%, by weight. When the fabric-adhesive agent is comprised exclusively of an anionic or nonionic detergent compound, such detergent is present in the carriers in an amount from about 0.2 to less than 5%, by weight, and preferably from about 1 to below 5%, by weight.

40 The useful primary, secondary and tertiary amines and their water-soluble salts are generally of the formula  $\text{R}^1\text{R}^2\text{R}^3\text{N}$ , wherein  $\text{R}^1$  represents an alkyl or alkenyl group containing from about 8 to 22 carbon atoms and  $\text{R}^2$  and  $\text{R}^3$  each represent hydrogen or hydrocarbyl groups containing from 1 to 22 carbon atoms, the term "hydrocarbyl group" encompassing alkyl, alkenyl, aryl and alkaryl groups including substituted groups of this type, common substituents being 45 hydroxy and alkoxy groups.

Within the general description of amines given above, specific examples include primary tallow amine, primary coconut amine, secondary tallow methyl amine, tallow dimethyl amine, tritallow amine, primary tallow amino hydrochloride, and primary coconut amine hydrochloride.

The useful diamine and diaminonium salts have the general formulas:  $\text{R}^1\text{R}^2\text{NR}^3\text{NR}^4\text{R}^5$ ;  $[\text{R}^1\text{R}^2\text{NR}^3\text{NR}^4\text{R}^5]^+ \cdot \text{X}^-$ ;  $[\text{R}^1\text{R}^2\text{NR}^3\text{NR}^4\text{R}^5]^+ \cdot \text{X}^-$ ; wherein  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are as defined above,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  have the same definition as  $\text{R}^2$  and  $\text{R}^3$ , and  $\text{R}^6$  represents an alkylene chain having from 4 to 6 carbon atoms wherein the middle carbon atoms may be linked to each other by an ether oxygen or by a double or triple bond.  $\text{X}^-$  represents an anion, preferably chloride, bromide, sulphate, methyl 55 sulphate or similar anion.

Specific examples of diamines and diamine salts include N-coco-1,3-diaminopropane, N-tallow-1,3-diaminopropane, N-oleyl-1,3-diaminopropane, N-tallow-1,3-diaminopropane diolate and N-tallow-1,3-diaminopropane diacetate.

Also suitable for use herein are the ethoxylated amine and diamine salts with fatty alkyl 60 groups of coconut, tallow and stearyl and containing from about 2 to 50 moles of ethylene oxide.

The useful quaternary ammonium compounds are generally of the formula  $[\text{R}^1\text{R}^2\text{R}^3\text{R}^4\text{N}]^+ \cdot \text{X}^-$ , wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{X}$  are as defined above,  $\text{R}^4$  represents an organic radical selected from among those defined for  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ . Although not indicated in the above formula,  $\text{R}^1$  and/or 65  $\text{R}^4$  may be attached to the quaternary nitrogen atom through an ether, alkoxy, ester or amide

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linkage. Among the quaternary ammonium compounds known to add substantivity to fabrics, particularly fabrics containing substantial amounts of cotton, three basic types are particularly useful for the present invention: (1) alkyl dimethyl ammonium compounds; (2) amido alkoxy-lated ammonium compounds; and (3) alkyl amido imidazolinium compounds. A detailed 5 description of these three types of compounds is set forth by R. Egan in *Journal American Oil Chemists' Society*, January, 1978 (Vol. 55), pages 118-121, such disclosure being incorporated herein by reference.

Long chain quaternary ammonium compounds are generally preferred for use herein, namely, 10 compounds wherein the number of carbon atoms is greater than eight. Within the more general description provided above concerning quaternary ammonium compounds useful for the present invention, preferred specific quaternary ammonium compounds include di-hydrogenated tallow dimethyl ammonium methyl sulphate; di-hydrogenated tallow dimethyl ammonium chloride, and 1-methyl-1-alkylamidoethyl-2-alkylimidazolinium methyl sulphate wherein the "alkyl groups" are oleyl or saturated hydrocarbyl groups derived from tallow or hydrogenated tallow. Dimethyl alkyl 15 benzyl quaternary compounds that are useful include those wherein the alkyl group is of a mixture of alkyl groups of 10 to 18 carbon atoms or 12 to 16 carbon atoms, e.g. lauryl, myristyl and palmityl. The various materials mentioned above are available commercially from various manufacturers, those from Sherex Chemical Company being identified by trademarks such as Adogen; Arosurf; Variquat; and Varisoft.

20 The quaternary ammonium salts employed herein are preferably substantially free of a conductive salt; the term "conductive salt" being used herein to refer to salts which are electrically conductive in aqueous solution. The conductive salts generally have a cation-anion bond of at least 50% ionic character as calculated in accordance with the method described in Pauling, "The Nature of the Chemical Bond", 3rd Edition, 1960. By use of the term 25 "substantially free" is meant a concentration of conductive salt less than that present at normal impurity levels in the quaternary ammonium compound. Generally, the concentration of conductive salt is below 1%, by weight.

The perfume-containing carriers of the invention are prepared by methods wherein the carrier particles are initially contacted with the perfume to be employed such that the major portion, 30 preferably substantially all, of such perfume is adsorbed and/or absorbed by such particles. The resulting perfume-containing particles are then contacted with the fabric adhesive agent such that substantially all of such fabric adhesive agent is adsorbed upon the surface of the particles and forms at least a partial coating thereupon.

A preferred technique for contacting the carrier particles with perfume consists of spraying the 35 perfume upon the surface of the particles. This may be effected, for example, by spraying the perfume from a pressurized nozzle so as to produce droplets which contact the surface of the particles, the latter being conveniently on a moving belt, such as, a conveyor belt. Alternatively, the process may be conveniently carried out by spraying the perfume over particles which are contained in a rotary drum or tube inclined at a slight angle, such as, from about 5° to 15°, the 40 rotational speed of such drum or tube being suitably from about 5 to 100 rpm. The range of suitable droplet size for effective spraying may vary from about 10 to about 200 microns in diameter, but preferably should be as small as possible relative to the diameter of the particles being sprayed.

The step of contacting the clay particles with the fabric adhesive agent may be carried out 45 using the same methods described above with regard to perfume sorption upon the carrier particles. Thus, for example, a solution or suspension of an anionic or nonionic detergent compound may be sprayed upon the surface of the particles to form a coating thereon. Where the fabric adhesive agent is a cationic compound, and the carrier particles comprise a clay mineral such as a smectite clay, it is important that the deposition of such compound is effected 50 under conditions which minimize the likelihood of an ion exchange reaction between the clay and the cationic compound. Accordingly, the method of contacting the clay mineral particles with a cationic compound is primarily concerned with avoiding the transformation of a major portion of the clay to a clay complex by an ion exchange reaction, thereby excluding, for example, the methods of preparing a "QA clay" and an "organo-clay complex" referred to in 55 U.S. Patent Nos. 3,948,790 and 4,292,035, respectively. To promote the adsorption of a cationic compound upon the surface of the clay particles, process conditions which favour swelling of the clay are generally avoided so as to minimize the likelihood of an undesired exchange reaction. Swelling of the clay is particularly favoured in an aqueous slurry, hence, the 60 less water which contacts the clay, the less the likelihood of effecting a cation exchange reaction. Accordingly, the weight of aqueous solvent which contacts the clay is generally restricted to an amount less than the weight of the clay, preferably below 50%, and more preferably below 25%, by weight, of such clay.

A preferred method of preparation comprises spraying the surface of the clay particles with a substantially non-aqueous solution or suspension containing the cationic compound, the 65 concentration of water in such solution or suspension being maintained generally below about

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50%, by weight, and preferably below about 10%, by weight. This is conveniently effected by spraying the solution or suspension of cationic compounds from a pressurized nozzle as described above. Spraying is preferably carried out at ambient temperatures and generally below 100°F (38°C). At temperatures above 100°F (38°C), particularly above 140°F (60°C), the 5 cationic compounds may be undesirably absorbed into the clay particles. Any organic solvent in which the cationic compound can be dispersed may be conveniently employed to form a solution or suspension for contacting the clay particle. Useful solvents include propylene glycol, hexylene glycol, ethanol and isopropyl alcohol.

In an alternative process of preparation, the particles of clay mineral or zeolite are placed on a 10 vibrating conveyor belt which is continuously wetted with a solution or suspension of a cationic compound, the effect of the vibration being to impart at least a partial coating of the cationic solution or suspension upon the surface of the particles.

In accordance with another embodiment of the present invention, finely divided particles as described above are bonded to the surface of a granular detergent composition which is devoid 15 of a soap to form agglomerate particles consisting of detergent-base granules encapsulated within a surface coating of a clay mineral. The agglomerate particles are characterised by an inner portion consisting of the detergent-base granules, and a surface portion contacting and surrounding such inner portion consisting essentially of particles containing at least about 75%, by weight, and preferably greater than about 90%, by weight, of a clay mineral and/or a zeolite 20 and less than about 5%, by weight, of surface active detergent compounds other than cationic detergents, preferably substantially free of such surfactants.

To achieve a substantially continuous external surface of the clay mineral on the agglomerate particles, the carrier particles employed are as small as possible relative to the detergent-base granules, allowing the particles to be closely packed around the granules. The detergent 25 composition granules are preferably spray-dried particles having sizes within mesh Nos. 8 to 100, U.S. Sieve Series (which have openings 2380 to 149 microns across). The carrier particles are preferably sufficiently small that they pass through a No. 325 mesh screen, U.S. Sieve Series (which has openings 44 microns across). The weight ratio of detergent composition granules to clay-containing particles may vary from about 10:1 to about 1:2, preferably from 30 about 5:1 to 1:1. The application of the particles to the base detergent granules may be effected by standard agglomeration techniques and equipment. One method that has been found to be especially useful is to mix the desired weights of the detergent composition granules and finely divided clay powder and while mixing, spray water on to the moving surfaces thereof, or more preferably, spray a dilute sodium silicate solution. Spraying may be carried out at room 35 temperature and should be gradual enough so as to prevent any objectionable lumping of the mixture. Mixing will continue in this manner until the clay particles all adhere to the detergent-base granules, after which mixing may be halted and the product may be screened or otherwise classified to be within the desired product size range. The silicate solution employed is normally at a concentration of about 0.05 to 10%, by weight, typically from about 1 to 6%, by weight.

40 The amount of silicate solution applied to the detergent-base granules generally constitutes from about 0.01 to about 2%, by weight. Satisfactory agglomeration and surface coating are obtained at such concentration using suitable agglomerating equipment, such as an O'Brien agglomerator, or a conventional inclined drum equipped with spray nozzles and baffles. The silicate concentration should not be so high as to inhibit dispersion of the softening particles in 45 the wash solution when the product is employed in laundry operations. Although it is preferred that silicate be employed in the agglomerating spray, useful product is obtainable by utilizing water alone as an agglomerating or binding agent or by employing aqueous solutions of other binders, such as gum, resins and surface active agents.

The sorption of the fabric adhesive agent and perfume upon the surface of the agglomerate 50 particle is carried out using the same methods described above with regard to the preparation of the carriers of the present invention. The resulting agglomerate particles are useful laundry products in which the detergent-base granule dissolves and functions in the standard manner in the wash solution while the particles of clay or zeolite become dispersed in the wash solution where they serve as perfume-containing carriers in accordance with the present invention.

55 The laundry detergent compositions with which the present perfume-containing carriers may be incorporated or with which it may be employed may contain one or more surface active agents selected from the group consisting of anionic, nonionic, cationic, amphoteric and zwitterionic detergents. The synthetic organic detergents employed in the practice of the invention may be any of a wide variety of such compounds which are well known and are 60 described at length in the text "Surface Active Agents and Detergents", Vol. II, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, the relevant disclosures of which are hereby incorporated by reference.

Among the anionic surface active agents useful in the present invention are those surface active compounds which contain an organic hydrophobic group containing from about 8 to 26 65 carbon atoms and preferably from about 10 to 18 carbon atoms in their molecular structure and

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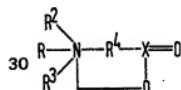
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- at least one water-solubilizing group selected from the group of sulphonate, sulphate, carboxylate, phosphonate and phosphate so as to form a water-soluble detergent.
- Examples of suitable anionic detergents include soaps, such as, the water-soluble salts (e.g. the sodium, potassium, ammonium and alkanolammonium salts) of higher fatty acids or resin 5 salts containing from about 8 to 20 carbon atoms and preferably 10 to 18 carbon atoms.
- Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, for example, tallow, grease, coconut oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, for example, sodium coconut soap and potassium tallow soap.
- 10 The anionic class of detergents also includes the water-soluble sulphated and sulphonated detergents having an aliphatic, preferably an alkyl, radical containing from about 8 to 26, and preferably from about 12 to 22 carbon atoms. (The term "alkyl" includes the alkyl portion of the higher acyl radicals.) Examples of the sulphonated anionic detergents are the higher alkyl mononuclear aromatic sulphonates such as the higher alkyl benzene sulphonates containing 15 from about 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, such as, for example, the sodium, potassium and ammonium salts of higher alkyl benzene sulphonates, higher alkyl toluene sulphonates and higher alkyl phenol sulphonates.
- Other suitable anionic detergents are the olefin sulphonates including long chain alkene 20 sulphonates, long chain hydroxyalkane sulphonates or mixtures of alkene sulphonates and hydroxyalkane sulphonates. The olefin sulphonate detergents may be prepared in a conventional manner by the reaction of sulphur trioxide ( $\text{SO}_3$ ) with long chain olefins containing from about 8 to 25, and preferably from about 12 to 21 carbon atoms, such olefins having the formula  $\text{RCH}=\text{CHR}'$  wherein R represents a higher alkyl group of from about 6 to 23 carbons and R' represents an alkyl group containing from about 1 to 17 carbon atoms, or hydrogen to form a mixture of sultones and alkene sulphonic acids which is then treated to convert the sultones to 25 sulphonates. Other examples of sulphate or sulphonate detergents are paraffin sulphonates containing from about 10 to 20 carbon atoms, and preferably from about 15 to 20 carbon atoms. The primary paraffin sulphonates are made by reacting long chain alpha olefins and bisulphites. Paraffin sulphonates having the sulphonate group distributed along the paraffin 30 chain are shown in U.S. Nos. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent No. 735,096.
- Other suitable anionic detergents are sulphated ethoxylated higher fatty alcohols of the 35 formula  $\text{RO}(\text{C}_2\text{H}_4\text{O})_n\text{SO}_3\text{M}$ , wherein R represents a fatty alkyl group of from 10 to 18 carbon atoms, m is from 2 to 6 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in the R group) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanolamino, or a higher alkyl benzene sulphonate 40 wherein the higher alkyl group is of 10 to 15 carbon atoms. The proportion of ethylene oxide in the polyethoxylated higher alkanol sulphate is preferably 2 to 5 moles of ethylene oxide groups per mole of anionic detergent, with three moles being most preferred, especially when the higher alkanol is of 11 to 15 carbon atoms. To maintain the desired hydrophilic-lipophile balance, when the carbon atom content of the alkyl chain is in the lower portion of the 10 to 18 carbon atom range, the ethylene oxide content of the detergent may be reduced to about two moles per mole whereas when the higher alkanol is of 16 to 18 carbon atoms in the higher part of the range, the number of ethylene oxide groups may be increased to 4 or 5 and in some cases to as high as 8 or 9. Similarly, the salt-forming cation may be altered to obtain the best 45 solubility. It may be any suitably solubilizing metal or radical but will most frequently be an alkali metal, e.g. sodium, or ammonium. If lower alkylamines or alkanolamine groups are utilized the alkyl groups and alkanols will usually contain from 1 to 4 carbon atoms and the amines and alkanolamines may be mono-, di- and tri-substituted, as in monoethanolamine, di-isopropanolamine and trimethylamine. A preferred polyethoxylated alcohol sulphate detergent is available 50 from Shell Chemical Company and is marketed as Neodol (Registered Trade Mark) 25-3S.
- The most highly preferred water-soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and tri-ethanolamine), alkali metal (such as, sodium and potassium) and alkaline earth metal (such as, calcium and magnesium) salts of the higher 55 alkyl benzene sulphonates, olefin sulphonates and higher alkyl sulphates. Among the above-listed anionics, the most preferred are the sodium linear alkyl benzene sulphonates (LABS), and especially those wherein the alkyl group is a straight chain alkyl radical of 12 or 13 carbon atoms.
- The nonionic synthetic organic detergents are characterised by the presence of an organic 60 hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic or alkyl aromatic hydrophobic compound with ethylene oxide (hydrophilic in nature). Practically any hydrophobic compound having a carboxy, hydroxy, amido or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic 65 detergent. The length of the hydrophilic or polyoxyethylene chain can be readily adjusted to

achieve the desired balance between the hydrophobic and hydrophilic groups.

- The nonionic detergent employed is preferably a poly-lower alkoxylated higher alkanol wherein the alkanol is of 10 to 18 carbon atoms and wherein the number of moles of lower alkylene oxide (of 2 or 3 carbon atoms) is from 3 to 12. Of such materials it is preferred to employ those 5 wherein the higher alkanol is a higher fatty alcohol of 11 to 15 carbon atoms and which contain from 5 to 9 lower alkoxy groups per mole. Preferably, the lower alkoxy group is ethoxy but in some instances it may be desirably mixed with propoxy, the latter, if present, usually being a minor (less than 50%) constituent. Exemplary of such compounds are those wherein the alkanol is of 12 to 15 carbon atoms and which contain about 7 ethylene oxide groups per mole, e.g. 10 Neodol (Registered Trade Mark) 25-7 and Neodol 23-6.5, which products are made by Shell Chemical Company, Inc. The former is a condensation product of a mixture of higher fatty alcohols averaging about 12 to 15 carbon atoms, with about 7 moles of ethylene oxide and the latter is a corresponding mixture wherein the carbon atom content of the higher fatty alcohol is 12 to 13 and the number of ethylene oxide groups per mole averages about 6.5. The higher 15 alcohols are primary alkanols. Other examples of such detergents include Tergitol (Registered Trade Mark) 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxylates made by Union Carbide Corporation. The former is a mixed ethoxylation product of an 11 to 15 carbon atom linear secondary alkanol with seven moles of ethylene oxide and the latter is a similar product but with nine moles of ethylene oxide being reacted. Also useful in the present 20 compositions are the higher molecular weight nonionic detergents, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, the higher fatty alcohol being of 14 to 15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products are also made by Shell Chemical Company.

Zwitterionic detergents such as the betaines and sulphobetaines having the following formula 25 are also useful:



wherein R represents an alkyl group containing from about 8 to 18 carbon atoms, R<sup>2</sup> and R<sup>3</sup> 30 each independently represent an alkyl or hydroxyalkyl group containing about 1 to 4 carbon atoms, R<sup>4</sup> represents an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms, and X represents a carbon atom or an S:O group. The alkyl group can contain one or more intermediate linkages such as amido, ether, or polyether linkages or nonfunctional substituents such as hydroxyl or halogen which do not substantially affect the hydrophobic character of the 35 R group. When X represents a carbon atom, the detergent is called a betaine; and when X represents an S:O group, the detergent is called a sulphobetaine or sulfatine.

Cationic surface active agents may also be employed. They comprise surface active detergent 40 compounds which contain an organic hydrophobic group which forms part of a cation when the compound is dissolved in water, and an anionic group. Typical cationic surface active agents are 45 amine and quaternary ammonium compounds.

Examples of suitable synthetic cationic detergents include: normal primary amines of the formula RNH<sub>2</sub> wherein R represents an alkyl group containing from about 12 to 15 atoms; diamines having the formula RNHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub> wherein R represents an alkyl group containing from about 12 to 22 carbon atoms, such as N-2-aminoethyl-stearyl amine and N-2-amino-ethyl 50 myristyl amine; amide-linked amines such as those having the formula R'CONHC<sub>2</sub>H<sub>4</sub>NH<sub>2</sub> wherein R' represents an alkyl group containing about 8 to 20 carbon atoms, such as N-2-amino ethylstearyl amide and N-amino ethylmyristyl amide; quaternary ammonium compounds 55 wherein typically one of the groups linked to the nitrogen atom is an alkyl group containing about 8 to 22 carbon atoms and three of the groups linked to the nitrogen atom are alkyl groups which contain 1 to 3 carbon atoms, including alkyl groups bearing inert substituents, such as phenyl groups, and there is present an anion such as halogen, acetate or methosulphate. The alkyl group may contain intermediate linkages such as amide which do not substantially affect the hydrophobic character of the group, for example, stearyl amido propyl quaternary ammonium chloride. Typical quaternary ammonium detergents are ethyl-dimethyl- 60 stearyl-ammonium chloride, benzyl-dimethyl-stearyl ammonium chloride, trimethyl-stearyl ammonium chloride, trimethyl-cetyl ammonium bromide, dimethyl-ethyl-lauryl ammonium chloride, dimethyl-propyl-myristyl ammonium chloride, and the corresponding methosulphates and acetates.

Amphoteric detergents are also suitable for the invention. Amphoteric detergents are well 65 known in the art and many operable detergents of this class are disclosed by Schwartz, Perry

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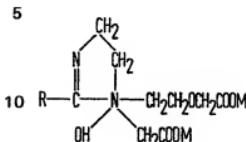
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and Berch in the aforementioned "Surface Active Agents and Detergents". Examples of suitable amphoteric detergents include: alkyl betaminodipropionates,  $RN(C_2H_4COOM)_2$ ; alkyl beta-amino propionates,  $RN(H)C_2H_4COOM$ ; and long chain imidazole derivatives having the general formula:



15 wherein in each of the above formulae R represents an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion. Specific operable amphoteric detergents include the disodium salt of undecylcyloimidinium-ethoxyethionic acid-2-ethionic acid, dodecyl beta alanine, and the inner salt of 2-trimethylamino lauric acid.

20 The detergent compositions of the invention optionally contain a detergent builder of the type commonly used in detergent formulations. Useful builders include any of the conventional inorganic water-soluble builder salts, such as, for example, water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, silicates, carbonates, and the like. Organic builders include water-soluble phosphonates, polyphosphonates, polyhydroxysulphonates, polycetates, carboxylates, polycarboxylates, succinates and the like.

25 Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, pyrophosphates and hexametaphosphates. The organic polyphosphonates specifically include, for example, the sodium and potassium salts of ethane-1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane-1,1,2-triphosphonic acid. Examples of these 30 and other phosphorous builder compounds are disclosed in U.S. Patent Nos. 3,213,030; 3,422,021; 3,422,137 and 3,400,176. Pentasodium tripolyphosphate and tetrasodium pyrophosphate are especially preferred water-soluble inorganic builders.

35 Specific examples of non-phosphorous inorganic builders include water-soluble inorganic carbonate, bicarbonate and silicate salts. The alkali metal, for example, sodium and potassium, carbonates, bicarbonates and silicates are particularly useful herein.

Water-soluble organic builders are also useful. For example, the alkali metal, ammonium and substituted ammonium acetates, carboxylates, polycarboxylates and polyhydroxysulphonates are useful builders for the compositions and processes of the present invention. Specific examples of acetate and polycarboxylate builders include sodium potassium, lithium, ammonium and 40 substituted ammonium salts of ethylene diaminetetraacetic acid, nitrilotriacetic acid, benzene polycarboxylic (i.e. penta- and tetra-) acids, carboxymethoxysuccinic acid and citric acid.

Water-insoluble builders may also be used, particularly, the complex silicates and more particularly, the complex sodium alumino silicates such as, zeolites, e.g. zeolite 4A, a type of zeolite molecule wherein the univalent cation is sodium and the pore size is about 4 Angstroms.

45 The preparation of such type of zeolite is described in U.S. Patent 3,114,603. The zeolites may be amorphous or crystalline and have water of hydration as known in the art.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

## 50 EXAMPLES 1A to 1C

Example 1A. This is a comparison example.

Agglomerates of Thixojel No. 1 clay were used in the present example and were prepared by the procedure described below wherein the following components were used: Thixojel No. 1 clay (325 mesh) and an aqueous agglomerating solution containing 7% of sodium silicate 55 having a ratio of  $\text{Na}_2\text{O}:\text{SiO}_2$  of about 1:2.4. Thixojel is the trademark of a Wyoming bentonite clay sold by Georgia Kaolin Co., Elizabeth, New Jersey.

The agglomerates were prepared in a rotary drum characterised by a 19.5 inch (49.5 cms) diameter, a 23.5 inch (59.7 cms) length and an axis of rotation adjustable between ten and ninety degrees from the vertical.

60 9.1 Kg of Thixojel No. 1 clay was charged into the above-described rotary drum which was aligned at an angle of 20 degrees from the vertical. 3.2 Kg of the aqueous silicate solution at a temperature of 43°C was sprayed on to the clay while the drum was rotating at about 6 rpm. The axis of the rotary drum was then adjusted to an angle of 70 degrees from the vertical and an additional 3.2 kg of silicate solution was sprayed on to the clay. The resulting wet 65 agglomerates of clay were transferred in 2 kg portions to an Aeromatic ST-5 (tradename) fluid

bed dryer, manufactured by Aeromatic Corp., Summerville, New Jersey, and dried to approximately 10 wt % moisture using an air flow rate of about 6,000 litres per minute and an air inlet temperature of 71°C. Drying was effected in about 15 minutes. The dried material was then passed through a Stokes granulator having a 40 mesh screen (U.S. Sieve Series) (which has 5 openings 420 microns across), the product particle size being between 40–100 mesh (420–149 microns). The fines passing through a 100 mesh (149 microns) screen were recycled to the rotary drum.

A spray dried granular unperfumed detergent composition was used as a component of the formulation described below and had the following composition:

Component	Weight Percent	
Sodium tridecyl benzene sulphonate	15	
15 Sodium tripolyphosphate	33	15
Sodium silicate (1 Na <sub>2</sub> O : 2.4 SiO <sub>2</sub> )	7	
Sodium carbonate	5	
Borax	2	
Sodium sulphate	27.8	
20 Carboxymethyl cellulose	0.2	20
Moisture	10	

100 grams of the above-described unperfumed detergent composition was blended with 0.2 g of a conventional detergent-type perfume based on limonene, geraniol, citral, cedrol, benzyl acetate, p-t-butyl cyclohexyl acetate and other aromatic ingredients in a Twin-Shell blender for ten minutes at a blender speed of about 20 rpm.

Example 1B. This is a comparison example.  
30 80 g of the unperfumed detergent composition described above was blended with 0.2 g of the same perfume employed in Example 1A in accordance with the procedure described above. 19.8 g of agglomerated Thixojel No. 1 as prepared above in Example 1A was then added to the blender and mixed with the contents thereof for about 10 minutes at a blender speed of about 20 rpm.

35 Example 1C  
19.8 g of agglomerated Thixojel No. 1 is blended for about 10 minutes with 0.2 g of the same perfume used in the formulations of Examples 1A and 1B in the Twin-Shell blender referred to in Example 1A. The resulting perfume-containing Thixojel clay is then put into a one-litre laboratory model drum which is rotated by a motor at about 10 rpm. Varisoft 3690 is then added dropwise to the clay while the drum is rotating so as to stimulate in the laboratory-scale equipment the effect of spraying the QA compound upon the clay. Varisoft 3690 is methyl(1-octoyl amido ethyl(2)oleyl imidazolinium-methyl sulphate (75% active ingredients in 25% isopropanol) manufactured by Sherek Chemical Company, Dublin, Ohio. The amount of QA compound 40 added to the particles relative to the weight of clay (based on the active ingredient in the Varisoft 3690) is 0.15 g/10g clay. The resulting agglomerates of clay are then removed from the rotating drum and mixed for about 10 minutes in a blender with 80g of the unperfumed 45 detergent composition described above in Example 1A.

Accordingly, the formulation of Example 1A represents a typical conventional detergent 50 formulation containing perfume; the formulation of Example 1B represents a detergent formulation similar to that of Example 1A but which in addition contains clay agglomerates; and the formulation of Example 1C represents a detergent formulation containing the perfume-containing carrier of the present invention.

Perfume tests are carried out using cotton, Dacron polyester, and Dacron polyester/cotton 55 (65/35) swatches and terry towels which are washed in a conventional U.S. washing machine at 25°C using water having a hardness of 100 ppm as calcium carbonate. Each of three sets of the above-described swatches are separately washed using 100 g of the formulations of Examples 1A, 1B and 1C, a different formulation being used for each washing.

Then the washing procedure is completed, the swatches are evaluated and the fabrics washed 60 in the formulation of Example 1C are found to retain the most perfume fragrance relative to the fabrics washed in the formulations of Examples 1A and 1B.

Based on the above, the use of the perfume-containing carrier of the present invention in a granular detergent composition results in a significant increase in the retention of a perfume fragrance on the laundered fabrics.

**EXAMPLES 2A to 2C**

The perfume tests described in Examples 1A to 1C are repeated using 100 g of each of the formulations for each washing as described in the examples except that in the formulation of Example 1C, instead of adding Varisoft 3690 to the perfume-containing Thixojel clay, there is 5 added primary tallow amine.

When the washing procedure is completed, the swatches are evaluated and the fabrics washed in the formulation of Example 1C are found to have a stronger perfume fragrance than the fabrics washed in the formulations of Examples 1B and 1C.

Improved perfume fragrance is achieved when the above-described perfume test is repeated 10 using instead of primary tallow amine, one of the following amines, diamines and diamine salts to coat the Thixojel clay in the formulation of Example 1C: secondary tallow methyl amine (Example 3), tritallow amine (Example 4), N-coco-1,3-diaminopropane (Example 5), N-tallow-1,3-diaminopropane (Example 6) and N-tallow-1,3-diaminopropane diacetate (Example 7).

**15 CLAIMS**

1. A perfume-containing carrier comprising (i) discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume, the said perfume being adsorbed or absorbed or adsorbed and absorbed on the said particles; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a 20 nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammmonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of surface active detergent compounds other than cationic detergents.

2. A carrier as claimed in Claim 1 in which the said fabric adhesive agent is a quaternary ammonium compound.

3. A carrier as claimed in Claim 2 in which the said quaternary ammonium compound contains more than eight carbon atoms.

30 4. A carrier as claimed in Claim 1, 2 or 3 in which the amount of the said quaternary ammonium compound is from about 0.2 to 16%, by weight.

5. A carrier as claimed in Claims 1, 2, 3 or 4 in which the weight of the said fabric adhesive agent is from about 0.2 to less than about 5%, by weight.

6. A carrier as claimed in any one of Claims 1 to 5 in which the weight ratio of the clay mineral and/or zeolite to perfume in the said carrier is from about 10:1 to about 200:1.

35 7. A carrier as claimed in any one of Claims 1 to 6 in which the weight of perfume is from about 0.2 to about 10%, by weight.

8. A carrier as claimed in any one of Claims 1 to 7 in which the said particles contain a smectite-type clay.

40 9. A carrier as claimed in any one of Claims 1 to 8 in which the said particles contain a bentonite clay.

10. A carrier as claimed in any one of Claims 1 to 9 in which the said particles contain a zeolite.

45 11. A carrier as claimed in any one of Claims 1 to 10 in which the said particles contain at least 90%, by weight, of the said clay mineral and/or zeolite.

12. A carrier as claimed in Claim 1 substantially as specifically described herein with reference to Example 1C, 2C or 3 to 7.

13. A particulate laundry detergent composition comprising:

(a) from about 0.1 to about 50%, by weight, of a perfume-containing carrier comprising (i) 50 discrete particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; (ii) a perfume; and (iii) a fabric-adhesive agent comprising at least one of an anionic detergent compound, a nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammmonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the said particles and forming at least a partial coating upon the surface thereof, the perfume-containing carrier containing less than about 5%, by weight, of detergent compounds other than cationic detergents;

(b) from about 2 to about 50%, by weight, additional to any detergent compound in the said 60 carrier, of one or more surface active detergent compounds selected from the group consisting of anionic, non-ionic, cationic, amphotropic and zwitterionic detergent compounds;

(c) from about 0 to about 70%, by weight, of a detergent builder salt; and

(d) the balance comprising water and optionally a filler salt.

14. A particulate laundry detergent composition as claimed in Claim 13 in which the 65 perfume containing carrier is as claimed in any one of Claims 1 to 12.

15. A particulate laundry detergent composition as claimed in Claim 13 or Claim 14 in which the said perfume is adsorbed or absorbed or adsorbed and absorbed on the said particles.
16. A particulate laundry detergent composition as claimed in Claim 13, 14 or 15 which additionally contains a second perfume to supplement the fragrance provided by the said perfume-containing carrier. 5
17. A laundry detergent composition as claimed in any one of Claims 13 to 16 in which the said detergent builder salt is present in an amount of from about 5 to about 50%, by weight.
18. A composition as claimed in any one of Claims 13 to 17 in which the amount of fabric adhesive agent is from about 0.05 to about 2%, by weight, of the said detergent composition.
- 10 19. A particulate laundry detergent composition as claimed in Claim 13 substantially as specifically described herein with reference to any one of the examples.
20. A process for depositing perfume on fabrics during laundering which comprises contacting the stained and/or soiled fabrics to be laundered with an aqueous solution or dispersion which contains a perfume-containing carrier as claimed in any one of Claims 1 to 12.
- 15 21. A process for depositing perfume on fabrics during laundering which comprises contacting the stained and/or soiled fabrics to be laundered with an aqueous solution or dispersion which contains a particulate laundry detergent composition as claimed in any one of Claims 13 to 19. 15
22. A laundry detergent product comprising:
- 20 (a) agglomerate particles which contain as individual components thereof (i) particles containing at least 75%, by weight, of a zeolite or a clay mineral (other than talc) or a mixture thereof; and (ii) granules of a detergent composition devoid of a soap; each of the said agglomerate particles being comprised of an inner portion and a surface portion, the inner portion of the agglomerate particles being contiguous with and essentially surrounded by the surface portion, the said inner portion consisting essentially of the said granular detergent composition and the said surface portion consisting essentially of the said particles;
- (b) a perfume, the said perfume being adsorbed and/or absorbed on the surface portion of the said agglomerate particles; and
- (c) a fabric adhesive agent comprising at least one of an anionic detergent compound, a 30 nonionic detergent compound, or a cationic compound selected from the group consisting of primary, secondary and tertiary amines and their water-soluble salts, diamine and diammonium salts, and quaternary ammonium, phosphonium and sulphonium compounds, the said fabric-adhesive agent being in contact with the surface portion of the said agglomerate particles and forming at least a partial coating thereupon. 30
- 35 23. A laundry detergent product as claimed in Claim 22 in which the particles containing at least 75% by weight, of a zeolite or a clay mineral (other than talc) are carrier particles as claimed in any one of Claims 1 to 12.
24. A laundry product as claimed in Claim 22 or Claim 23 in which the said granules of detergent composition contain from about 2 to about 50%, by weight, of a surface active 40 detergent compound selected from the group consisting of anionic, nonionic, cationic, amphoteric and zwitterionic detergent compounds.
25. A laundry product as claimed in Claim 22, 23 or 24 in which the weight of perfume in the particles is from about 0.2 to about 10%, by weight.
26. A laundry product as claimed in Claim 22 substantially as specifically described herein 45 with reference to any one of the examples. 45



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US94/06050</p> <p>(22) International Filing Date: 31 May 1994 (31.05.94)</p> <p>(30) Priority Data: 08/071,124 2 June 1993 (02.06.93) US</p> <p>(71) Applicant: THE PROCTER &amp; GAMBLE COMPANY [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors: PAN, Robert, Ya-Lin; 5750 Samstone Court, Cincinnati, OH 45242 (US). YU, Jing-Feng; 5460 Fawnview Court, West Chester, OH 45069 (US). CARAVAJAL, Gregory, Stephen; 1586 Gelhot, #219, Fairfield, OH 45014 (US). GRAVES, Sharon, Anne; 19188 Far Drive, Lawrenceburg, OH 47025 (US). MUELLER, William, Richard; 2432 Swales Drive, Lawrenceburg, OH 47025 (US).</p> <p>(74) Agents: REED, T., David et al; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).</p>		<p>(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b>  <i>With international search report.  Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(64) Title: PERFUME DELIVERY SYSTEM COMPRISING ZEOLITES</p> <p>(57) Abstract</p> <p>Granular detergent compositions comprise conventional ingredients and a perfume delivery system which comprises Type X or Type Y Zeolites having a perfume releasably adsorbed within their pores, and a barrier matrix comprising a fluid polyol or diol which is insoluble with the perfume and a solid polyol containing more than three hydroxyl moieties. Methods of depositing said perfume onto fabric surfaces are disclosed.</p>			

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## PERFUME DELIVERY SYSTEM COMPRISING ZEOLITES

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FIELD OF THE INVENTION

The present invention relates to perfume delivery systems and  
10 methods of using said perfume delivery systems in detergent  
compositions, especially granular detergents.

BACKGROUND OF THE INVENTION

Most consumers have come to expect scented laundry products  
and to expect that fabrics which have been laundered also to have a  
15 pleasing fragrance. Perfume additives make laundry compositions  
more aesthetically pleasing to the consumer, and in some cases the  
perfume imparts a pleasant fragrance to fabrics treated therewith.  
However, the amount of perfume carry-over from an aqueous laundry  
bath onto fabrics is often marginal. Industry, therefore, has long  
20 searched for an effective perfume delivery system for use in  
laundry products which provides long-lasting, storage-stable  
fragrance to the product, as well as fragrance to the laundered  
fabrics.

Laundry and other fabric care compositions which contain  
25 perfume mixed with or sprayed onto the compositions are well known  
from commercial practice. Because perfumes are made of a combi-  
nation of volatile compounds, perfume can be continuously emitted  
from simple solutions and dry mixes to which the perfume has been  
added. Various techniques have been developed to hinder or delay  
30 the release of perfume from compositions so that they will remain  
aesthetically pleasing for a longer length of time. To date,  
however, few of the methods deliver significant fabric odor  
benefits after prolonged storage of the product.

Moreover, there has been a continuing search for methods and  
35 compositions which will effectively and efficiently deliver perfume  
from a laundry bath onto fabric surfaces. As can be seen from the  
following disclosures, various methods of perfume delivery have  
been developed involving protection of the perfume through the wash

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- cycle, with release of the perfume onto fabrics. U.S. Pat. 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents, including perfume, through the wash and dry cycle via a fatty quarternary ammonium salt. U.S. Pat. 4,402,856, Schnoring et al, issued Sept. 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of perfume out of the capsule only at certain temperatures. U.S. Pat. 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles to protect the perfume through storage in dry compositions and through the laundry process. The perfume assertedly diffuses through the wax on the fabric in the dryer. U.S. Pat. 5,066,419, Walley et al, issued Nov. 19, 1991, teaches perfume dispersed with a water-insoluble nonpolymeric carrier material and encapsulated in a protective shell by coating with a water-insoluble friable coating material. U.S. Pat. 5,094,761, Trinh et al, issued Mar. 10, 1992, teaches a perfume/cyclodextrin complex protected by clay which provides perfume benefits to at least partially wetted fabrics.
- Another method for delivery of perfume in the wash cycle involves combining the perfume with an emulsifier and water-soluble polymer, forming the mixture into particles, and adding them to a laundry composition, as is described in U.S. Pat. 4,209,417, Whyte, issued June 24, 1980; U.S. Pat. 4,339,356, Whyte, issued July 13, 1982; and U.S. Pat. No. 3,576,760, Gould et al, issued April 27, 1971. However, even with the substantial work done by industry in this area, a need still exists for a simple, more efficient and effective perfume delivery system which can be mixed with laundry compositions to provide initial and lasting perfume benefits to fabrics which have been treated with the laundry product.

The perfume can also be adsorbed onto a porous carrier material, such as a polymeric material, as described in U.K. Pat. Pub. 2,066,839, Bares et al, published July 15, 1981. Perfumes have also been adsorbed onto a clay or zeolite material which is then admixed into particulate detergent compositions. Generally, the preferred zeolites have been Type A or 4A Zeolites with a nominal pore size of approximately 4 Angstrom units. It is now

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believed that with Zeolite A or 4A, the perfume is adsorbed onto the zeolite surface with relatively little of the perfume actually absorbing into the zeolite pores. While the adsorption of perfume onto zeolite or polymeric carriers may perhaps provide some improvement over the addition of neat perfume admixed with detergent compositions, industry is still searching for improvements in the length of storage time of the laundry compositions without loss of perfume characteristics, in the intensity or amount of fragrance delivered to fabrics, and in the duration of the perfume scent on the treated fabric surfaces.

Another problem in providing perfumed products is the odor intensity associated with the products, especially high density granular detergent compositions. As the density and concentration of the detergent composition increase, the odor from the perfume components can become undesirably intense. A need therefore exists for a perfume delivery system which substantially releases the perfume odor during use but which does not provide an overly-intensive odor to the product, itself.

By the present invention it has now been discovered that certain zeolites with a nominal pore size of at least about 6 Angstroms effectively incorporate perfume into their pores. Without wishing to be limited by theory, it is believed that these zeolites provide a channel or cage-like structure in which the perfume molecules are trapped. Unfortunately, such perfumed zeolites are not sufficiently storage-stable for commercial use in granular fabric care products such as laundry detergents, particularly due to premature release of perfume upon moisture absorption. However, it has now also been discovered that the perfumed zeolite can then be matrixed with simple water-soluble, but perfume-insoluble, materials (such as sugars) which form a protective barrier entrapping and maintaining the perfume within the zeolite's pores. Thus, the perfume substantially remains in the matrix, even under humid conditions, without the need for expensive, complex coatings, encapsulations, or resin layers. It is also believed that since the perfume is incorporated into the relatively large zeolite pores, it has better perfume retention through the laundry process than other smaller pore size zeolites in which the perfume is predominately adsorbed on the zeolite

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surface. Fabrics treated by such perfume delivery systems thus have higher scent intensity and remain scented for longer periods of time after laundering.

The present invention solves the long-standing need for a simple, effective, storage-stable perfume delivery system which provides odor benefits during and after the laundering process, but which has reduced product odor during storage of the composition. The present invention, after removal of the matrix in the wash, provides the additional, unexpected benefit of continued odor release when exposed to heat or humidity while being stored, dried or ironed.

#### BACKGROUND ART

U.S. Patent 4,539,135, Ramachandran et al, issued September 3, 1985, discloses particulate laundry compounds comprising a clay or zeolite material carrying perfume. U.S. Patent 4,713,193, Tai, issued December 15, 1987, discloses a free-flowing particulate detergent additive comprising a liquid or oily adjunct with a zeolite material. Japanese Patent HEI 4[1992]-218583, Nishishiro, published August 10, 1992, discloses controlled-release materials including perfumes plus zeolites. U.S. Patent 4,304,675, Corey et al, issued December 8, 1981, teaches a method and composition comprising zeolites for deodorizing articles.

#### SUMMARY OF THE INVENTION

The present invention relates to a perfume delivery composition in the form of particles comprising:

- a) from about 10% to about 90%, preferably from about 60% to about 80%, by weight, of a solid, water-insoluble, porous carrier which comprises a natural or synthetic zeolite having a nominal pore size of at least about 6 Angstroms;
- b) a perfume which is releasably incorporated in the pores of said zeolite carrier to provide a perfumed zeolite; and
- c) from about 10% to about 90%, preferably from about 20% to about 40%, by weight, of a matrix coated on said perfumed zeolite which comprises a water-soluble (wash removable) composition in which the perfume is substantially insoluble, comprising from 0% to about 80%, by weight, of at least one solid polyol containing more than 3 hydroxyl

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moieties and from about 20% to about 100%, by weight, of a fluid diol or polyol in which the perfume is substantially insoluble and in which the solid polyol is substantially soluble.

5        The perfumed zeolite comprises from about 5% to about 30%, preferably from about 5% to about 20%, most preferably from about 7% to about 15%, by weight, of perfume and from about 70% to about 95%, preferably from about 80% to about 95%, most preferably from about 85% to about 93%, by weight, of zeolite. Preferred zeolites  
10      have a nominal pore size of at least about 6, preferably at least about 7 Angstroms, and a particle size no larger than about 120 microns, most preferably no larger than 30 microns. Preferred zeolites are faujasite-type zeolites selected from the group consisting of Zeolite X, Zeolite Y, and mixtures thereof. Typical,  
15      but non-limiting, examples of perfume ingredients employed in this invention include those selected from the group consisting of hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.

Preferred fluid diols and polyols used in the matrix are  
20      selected from the group consisting of glycerol, ethylene glycol, and diglycerol. Preferred solid polyols used in the matrix are selected from the group consisting of glucose, sorbitol, maltose, glucamine, sucrose, polyvinyl alcohol, starch, alkyl polyglycoside, sorbitan fatty ester, polyhydroxy fatty acid amides containing from about 1 to about 18, preferably from 1 to 12, most preferably from 1 to 8, carbon atoms in their fatty acid moieties, and mixtures thereof.

The perfume delivery particles are preferably in agglomerated form, said agglomerates being dissociable in water and having an average size of from about 200 microns to about 1000 microns, preferably from about 400 microns to about 600 microns. The agglomerated particles allow for admixing with detergent ingredients which have similar particle size.

35      The perfume delivery compositions herein can also be used in conventional detergent compositions, particularly in granular detergent compositions. The detergent composition will comprise from about 1% to about 20%, preferably from about 1% to about 8%, by weight, of said perfume delivery composition. The conventional

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detergent ingredients employed in fully-formulated detergent compositions provided herein can comprise from about 1% to about 99%, preferably from about 5% to about 80% of a detergents surfactant. Optionally, detergent compositions can comprise from  
5 about 5% to about 80% of a detergents builder. Other optional detergent ingredients can also be included in the fully-formulated detergent/perfume compositions provided by this invention. A second perfume can be sprayed onto the surface of said detergent granules, thereby providing fragrance to the product while it is  
10 stored.

The perfume delivery system of this invention is particularly effective in high density granular detergent compositions. Such concentrated granular detergent compositions typically have a bulk density of at least 550 grams/liter, preferably at least about 650  
15 grams/liter, and ranging as high as about 900 grams/liter.

The method for depositing perfume on fabrics comprises contacting fabrics with an aqueous liquor containing at least about 1 ppm of said perfume delivery composition and, optionally, at least about 100 ppm of conventional detergents ingredients. Preferably,  
20 the aqueous liquor contains from about 10 ppm to about 200 ppm, most preferably from about 10 ppm to about 80 ppm, of the perfume delivery composition. The invention also encompasses a method for providing odor benefits on fabrics during storage, drying, or ironing comprising contacting fabrics with an aqueous liquor  
25 containing at least about 1 ppm, preferably from about 10 ppm to about 200 ppm, most preferably from about 10 ppm to about 80 ppm, of said perfume delivery composition and, optionally, at least about 100 ppm of conventional detergents ingredients, and drying the fabric in an automatic dryer, applying heat to fabrics which have  
30 been line-dried or machine dried at low heat by conventional ironing means (preferably with steam or pre-wet), or storing fabrics which have been line-dried or machine dried at low heat under ambient conditions with humidity (above about 20%).

The perfume delivery composition can be prepared in an  
35 anhydrous system by a process which comprises the steps of:  
a) forming a perfumed zeolite by mixing porous, substantially dehydrated (less than 10%, preferably less than 5%,

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- water) Zeolite X or Y with a perfume such that the perfume is incorporated into the pores of the zeolite;
- 5        b) forming a matrix by mixing a solid polyol containing more than 3 hydroxyl moieties with a fluid polyol or diol such as glycerol, ethylene glycol, or diglycerol to form a liquid; and
- c) mixing the matrix (b) with the perfumed zeolite (a) until free flowing particles are formed.

All percentages, ratios, and proportions herein are on a  
10 weight basis unless otherwise indicated. All documents cited are hereby incorporated by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a perfume delivery system comprising a dehydrated zeolite, preferably Type X Zeolite, Type Y  
15 Zeolite, or a mixture thereof, wherein a perfume or a mixture of perfume and perfume fixative has been releasably absorbed in the pores of said zeolite. The perfumed zeolite is incorporated, in the absence of water, with a matrix preferably comprising a fluid diol or polyol and a solid polyol. The perfume delivery system is  
20 especially useful in granular detergent compositions.

The component materials are described below.

##### Perfume

As used herein the term "perfume" is used to indicate any pleasant smelling, odoriferous material which can be absorbed into  
25 the pores of the zeolites herein and which is subsequently released into the aqueous bath and/or onto fabrics contacted therewith. The perfume selected should be immiscible with the matrix materials employed in the perfume delivery system so as to limit loss of the perfume before use. The perfume will most often be liquid at  
30 ambient temperatures. A wide variety of chemicals are known for perfume uses, including materials such as aldehydes, ketones and esters. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes. The perfumes herein can be relatively simple in their compositions or can comprise highly sophisticated complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor. Typical perfumes can comprise, for example, woody/earthy bases containing  
35

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exotic materials such as sandalwood, civet and patchouli oil. The perfumes can be of a light floral fragrance, e.g., rose extract, violet extract, and lilac. The perfumes can also be formulated to provide desirable fruity odors, e.g., lime, lemon, and orange. Any 5 chemically compatible material which exudes a pleasant or otherwise desirable odor can be used in the perfumed compositions herein.

Examples of perfume ingredients deliverable by this invention include: hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.

10                   Perfume Fixative

Optionally, the perfume can be combined with a perfume fixative. The perfume fixative materials employed herein are characterized by several criteria which make them especially suitable in the practice of this invention. Dispersible, toxicologically-acceptable, non-skin irritating, inert to the perfume, degradable and/or available from renewable resources, and relatively odorless additives are used. Perfume fixatives are believed to slow the evaporation of more volatile components of the perfume.

Examples of suitable fixatives include members selected from 20 the group consisting of diethyl phthalate, musks, and mixtures thereof. If used, the perfume fixative comprises from about 10% to about 50%, preferably from about 20% to about 40%, by weight, of the perfume.

25                   Zeolites

The term "zeolite" used herein refers to a crystalline aluminosilicate material. The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure represented by



30 where n is the valence of the cation M, x is the number of water molecules per unit cell, m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100. Most preferably, y/m is 1 to 5. The cation M can be Group IA and Group IIA elements, such as sodium, potassium, magnesium, and calcium.

35 In general, the zeolite material useful in the present invention encompasses water-insoluble aluminosilicate particles with high adsorption efficiency, and a nominal pore size of at least about 6 Angstroms which is larger than the transverse axial

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dimension of the perfume and optional perfume fixative molecules that are to be absorbed in the porous material but which is capable of retaining the perfume in the zeolite structure while being stored. Pore volumes and pore size distributions may be measured by the recognized techniques of adsorption of sorbates of progressively increasing molecular diameter and by x-ray crystallography.

Contrary to the teachings of previous references, such as U.S. Pat. 4,304,675, and U.S. Pat. 4,539,135, both cited above, the use of Zeolite A or 4A is believed to have pore sizes too small (4 Angstroms or less) for effective absorption of the perfume molecules. Thus, it is believed that the perfume incorporated on type A or 4A Zeolites will rapidly dissipate from the zeolites during wash. Hence, compositions comprising such zeolites are not acceptable for effective carry-over of the perfume onto the fabrics which have been treated with them.

The preferred zeolite useful herein is a faujasite-type zeolite, including Type X Zeolite or Type Y Zeolite, both with a nominal pore size of about 8 Angstrom units, typically in the range of from about 7.4 to about 10 Angstrom units.

The aluminosilicate zeolite materials useful in the practice of this invention are commercially available. The zeolites useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. Methods for producing X and Y-type zeolites are well-known and available in standard texts. Preferred synthetic crystalline aluminosilicate materials useful herein are available under the designation Type X or Type Y.

For purposes of illustration and not by way of limitation, in a preferred embodiment, the crystalline aluminosilicate material is Type X and is selected from the following:

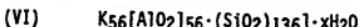
- (I)  $\text{Na}_{86}[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$ ,
- 35 (II)  $\text{K}_{86}[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$ ,
- (III)  $\text{Ca}_{40}\text{Na}_{6}[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$ ,

- 10 -



and mixtures thereof, wherein x is from about 0 to about 276.  
Zeolites of Formula (I) and (II) have a nominal pore size or  
5 opening of 8.4 Angstroms units. Zeolites of Formula (III) and (IV)  
have a nominal pore size or opening of 8.0 Angstroms units.

In another preferred embodiment, the crystalline aluminosilicate material is Type Y and is selected from the following:



and mixture thereof, wherein x is from about 0 to about 276.  
15 Zeolites of Formula (V) and (VI) have a nominal pore size or  
opening of 8.0 Angstroms units.

Zeolites used in the present invention are in particle form  
having an average particle size from about 0.5 microns to about 120  
microns, preferably from about 0.5 microns to about 30 microns, as  
20 measured by standard particle size analysis technique.

The size of the zeolite particles allows them to be entrained  
in the fabrics with which they come in contact. Once established  
on the fabric surface (with their coating matrix having been washed  
away during the laundry process), the zeolites can begin to release  
25 their perfume, especially when subjected to heat or humid  
conditions.

Incorporation of Perfume in Zeolite - Type X or Type Y  
Zeolites are first activated/dehydrated by heating to about  
150-350°C, optionally with reduced pressure (from about 0.001 to  
30 about 20 Torr), for at least 12 hours. After activation, the  
perfume is slowly and thoroughly mixed with the activated zeolite  
and, optionally, heated to about 600°C for about 2 hours to  
accelerate absorption equilibrium within the zeolite particles.  
The perfume/zeolite mixture is then cooled to room temperature and  
35 is in the form of a free-flowing powder.

#### Matrix

The matrix employed in the perfume delivery system of this  
invention comprises a fluid diol or polyol, such as glycerol,

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- ethylene glycol, or diglycerol (suitable fluid diols and polyols typically have a M.P. below about -100C) and, optionally but preferably, a solid polyol containing more than three hydroxyl moieties, such as glucose, sorbitol, and other sugars. The solid 5 polyol should be dissolvable with heating in the fluid diol or polyol to form a viscous (approximately 4000 cPs), fluid matrix (i.e., the consistency of honey). The matrix, which is insoluble with the perfume, is thoroughly mixed with the perfumed zeolite and, thereby, entraps and "protects" the perfume in the zeolite.
- 10 Solubility of the matrix in water enables the perfumed zeolite to be released in the aqueous bath during laundering.

The preferred properties of the matrix formed by the fluid diol or polyol and the solid polyol include strong hydrogen-bonding which enables the matrix to attach to the zeolite at the 15 siloxide sites and to compete with water for access to the zeolite; incompatibility of the matrix with the perfume which enables the matrix to contain the perfume molecules inside the zeolite cage and to inhibit diffusion of the perfume out through the matrix during dry storage; hydrophilicity of the matrix to enable the matrix 20 materials to dissolve in water for subsequent perfume release from the zeolites; and humectancy which enables the matrix to serve as a limited water sink to further protect the perfumed zeolite from humidity during storage.

The matrix material comprises from about 20% to about 100%, 25 preferably from about 50% to about 70%, by weight of the fluid diol or polyol and from 0% to about 80%, preferably from about 30% to about 50%, by weight, of one or more solid polyols. Of course, the proportions can vary, depending on the particular solid polyols and fluid polyols that are chosen. The perfume delivery system 30 comprises from about 10% to about 90%, preferably from about 20% to about 40%, by weight of the diol/polyol matrix material, the balance comprising the perfume-plus-zeolite.

In addition to its function of containing/protecting the 35 perfume in the zeolite particles, the matrix material also conveniently serves to agglomerate multiple perfumed zeolite particles into agglomerates having an overall particles size in the range of 200 to 1000 microns, preferably 400 to 600 microns. This reduces dustiness. Moreover, it lessens the tendency of the smaller,

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individual perfumed zeolites to sift to the bottom of containers filled with granular detergents, which, themselves, typically have particle sizes in the range of 200 to 1000 microns.

5 The following nonlimiting example describes a typical laboratory preparation of the perfume delivery composition.

EXAMPLE I

About 119 g of Zeolite 13X powder is activated/dehydrated at 200°C at 14 Torr for about 24 hours. The activated zeolite (119 g) is added to a glass vessel, and 21 g of perfume (any commercial 10 perfume is useful; Alba-C is typical) is slowly added with thorough mixing and shaking to yield an 85/15 zeolite:perfume ratio. The zeolite/perfume mixture is transferred to a mixer (Cuisinart) and mixed for approximately 20 seconds. The mixture is then returned to a glass vessel. The vessel is sealed and vibrated to compact 15 the sample. The zeolite/perfume mixture is heated in the closed vessel at 60°C for 2 hours, and then cooled to room temperature.

In another glass vessel, 34.3g of anhydrous glycerol is heated to approximately 110-120°C with continuous stirring. To the glycerol is added 25.7g of anhydrous glucose to yield a 42.5:57.5 20 ratio of glycerol to glucose. Heating and stirring are continued until a clear, liquid solution is formed. The solution is cooled to room temperature.

To a large, flat crystallizing dish, first add the 60g of glycerol/glucose solution, and then add the 140g of zeolite/perfume. The solid zeolite/perfume is thoroughly mixed with the viscous liquid solution and transferred to a Cuisinart mixer for approximately 3 minutes of agitation. The resulting product, which is in the form of a free-flowing powder agglomerate, is then transferred to a container and sealed for storage.

30 The perfume delivery compositions are used in compositions with deterutive ingredients, as follows.

Conventional Deterutive Ingredients

Deterutive Surfactant

35 The amount of deterutive surfactant included in the conventional detergent ingredients employed in the present invention can vary from about 1% to about 99% by weight of the detergent composition depending upon the particular surfactant(s) used and the effects desired. Preferably, the deterutive surfac-

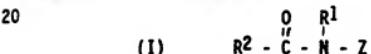
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tant(s) comprises from about 5% to about 80% by weight of the composition.

The detergentsurfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred detergent compositions, therefore, comprise anionic detergentsurfactants or mixtures of anionic surfactants with other surfactants disclosed herein.

Nonlimiting examples of surfactants useful herein include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates and primary, secondary, and random alkyl sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters, C<sub>12</sub>-C<sub>18</sub> alkyl and alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein: R<sup>1</sup> is H, C<sub>1</sub>-C<sub>8</sub> hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably C<sub>1</sub> alkyl (i.e., methyl); and  
25 R<sup>2</sup> is a C<sub>5</sub>-C<sub>32</sub> hydrocarbyl moiety, preferably straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, more preferably straight chain C<sub>9</sub>-C<sub>17</sub> alkyl or alkenyl, most preferably straight chain C<sub>11</sub>-C<sub>19</sub> alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of  
30 glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyLATED derivative (preferably ethoxyLATED or propoxyLATED) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycetyl moiety.  
35 Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the

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individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH<sub>2</sub>-

5 (CHOH)<sub>n</sub>-CH<sub>2</sub>OH, -CH(CH<sub>2</sub>OH)-(CHOH)<sub>n-1</sub>-CH<sub>2</sub>OH, -CH<sub>2</sub>-(CHOH)<sub>2</sub>(CHOR')-(CHOH)-CH<sub>2</sub>OH, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH<sub>2</sub>-(CHOH)<sub>4</sub>-CH<sub>2</sub>OH.

10 In surfactant formula (I), R<sup>1</sup> can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R<sup>1</sup> is preferably methyl or hydroxalkyl. If lower sudsing is desired, R<sup>1</sup> is preferably C<sub>2</sub>-C<sub>8</sub> alkyl, especially n-propyl, iso-propyl, n-butyl, 15 iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

R<sup>2</sup>-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc. (It is to be understood that separate portions of the poly- hydroxy fatty acid amides can be used both as the detergentsurfactant in 20 the detergent compositions herein, and as the solid polyol of the matrix material used to coat the preferred zeolites.)

#### Detergent Builders

Other conventional detergents optionally employed in the present invention include inorganic and/or organic detergent builders to assist in mineral hardness control. Typically, 25 these builders will comprise from about 5% to about 80% by weight of the detergent compositions.

Inorganic detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required 30 in some locales.

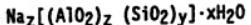
35 Examples of silicate builders are the alkali metal silicates, particularly those having a SiO<sub>2</sub>:Na<sub>2</sub>O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates

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described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application 5 No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Preferred aluminosilicates are zeolite builders which have the formula:



10 wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Such builders are Type A or 4A Zeolites, as distinguished from the Type X or Type Y Zeolites used to carry the perfume.

15 Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669; Krummel, et al., issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A and Zeolite P (B). Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

25 Organic detergents builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds, such as ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987.

30 Other useful detergency builders include the ether hydroxy-polycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid,

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oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders that can 5 also be used in detergent compositions, especially in combination with zeolite and/or layered silicate builders.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued 10 January 28, 1986.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium 15 orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

#### Optional Detergent Adjuncts

20 As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as detergents surfactants and detergents builders. Optionally, the detergent ingredients can include one or more other detergents adjuncts or other materials for assisting or 25 enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual detergents adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Such adjuncts which can be included in detergent compositions 30 employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 80% of the detergent ingredients, preferably from about 0.5% to about 20%), include color speckles, suds boosters, suds suppressors, anti-tarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, solvents, solubilizing agents, chelating agents, clay soil removal/anti-redeposition agents, polymeric 35

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dispersing agents, processing aids, fabric softening components, static control agents, bleaching agents, bleaching activators, bleach stabilizers, etc.

High Density Granular Detergent Composition

- 5        The perfume delivery composition can be used in both low density (below 550 grams/liter) and high density granular detergent compositions in which the density of the granule is at least 550 grams/liter. Such high density detergent compositions typically comprise from about 30% to about 90% of detergentsurfactant.
- 10      Low density compositions can be prepared by standard spray-drying processes. Various means and equipment are available to prepare high density granular detergent compositions. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density
- 15      less than about 500 g/l. Accordingly, if spray drying is used as part of the overall process, the resulting spray-dried detergent particles must be further densified using the means and equipment described hereinafter. In the alternative, the formulator can eliminate spray-drying by using mixing, densifying and granulating
- 20      equipment that is commercially available. The following is a nonlimiting description of such equipment suitable for use herein.

- High speed mixer/densifiers can be used in the present process. For example, the device marketed under the trademark "Lodige CB30" Recycler comprises a static cylindrical mixing drum having a central rotating shaft with mixing/cutting blades mounted thereon. Other such apparatus includes the devices marketed under the trademark "Shugi Granulator" and under the trademark "Drais K-TTP 80". Equipment such as that marketed under the trademark "Lodige KM600 Mixer" can be used for further densification.
- 30      In one mode of operation, the compositions are prepared and densified by passage through two mixer and densifier machines operating in sequence. Thus, the desired compositional ingredients can be admixed and passed through a Lodige mixture using residence times of 0.1 to 1.0 minute then passed through a second Lodige mixer using residence times of 1 minute to 5 minutes.

In another mode, an aqueous slurry comprising the desired formulation ingredients is sprayed into a fluidized bed of particulate surfactants. The resulting particles can be further

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densified by passage through a Lodige apparatus, as noted above. The perfume delivery particles are admixed with the detergent composition in the Lodige apparatus.

The final density of the particles herein can be measured by 5 a variety of simple techniques, which typically involve dispensing a quantity of the granular detergent into a container of known volume, measuring the weight of detergent and reporting the density in grams/liter.

Once the low or high density granular detergent "base" 10 composition is prepared, the agglomerated perfume delivery system of this invention is added thereto by any suitable dry-mixing operation.

#### Deposition of Perfume onto Fabric Surfaces

The method of washing fabrics and depositing perfume thereto 15 comprises contacting said fabrics with an aqueous wash liquor comprising at least about 100 ppm of conventional detergents ingredients described hereinabove, as well as at least about 1 ppm of the above-disclosed perfume delivery system. Preferably, said aqueous liquor comprises from about 500 ppm to about 20,000 ppm of 20 the conventional detergents ingredients and from about 10 ppm to about 200 ppm of the perfume delivery system.

The perfume delivery system works under all circumstances, but is particularly useful for providing odor benefits on fabrics during storage, drying or ironing. The method comprises con-25 tacting fabrics with an aqueous liquor containing at least about 100 ppm of conventional detergents ingredients and at least about 1 ppm of the perfume delivery composition such that the perfumed zeolite particles are entrained on the fabrics, storing line-dried fabrics under ambient conditions with humidity of at least 20%, 30 drying the fabric in a conventional automatic dryer, or applying heat to fabrics which have been line-dried or machine dried at low heat (less than about 50°C) by conventional ironing means (preferably with steam or pre-wetting).

The following nonlimiting examples illustrate the parameters 35 of and compositions employed within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

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EXAMPLE II

A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
5	C <sub>12</sub> linear alkyl benzene sulfonate	22
	Phosphate (as sodium tripolyphosphate)	30
	Sodium carbonate	14
	Sodium silicate	3
	Sodium percarbonate	5
10	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Sodium sulfate	5.5
	Perfume Delivery System (Example I)	3.0
	Nonanoyloxybenzenesulfonate	5
	Minors, filler* and water	Balance to 100%

15 \*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay, silicates, and the like.

An aqueous crutcher mix of heat and alkali stable components of the detergent composition is prepared and spray-dried. The other ingredients, including the perfume delivery system, are admixed in the final composition so that the composition contains the ingredients tabulated at the levels shown.

The detergent granules are added together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine to provide a detergent concentration of 1000 ppm in the 17 gallon (65 l) water-fill machine. Fabrics laundered with the composition and dried have a noticeable perfume fragrance. The fragrance intensity is still unchanged approximately 6 days after drying of the fabrics at 60-70°C for 40 minutes.

EXAMPLE III

30 A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
	Anionic alkyl sulfate	7
	Nonionic surfactant	5
35	Zeolite A (0.1-10 micron)	10
	Trisodium citrate	2
	SKS-6 silicate builder	10
	Acrylate maleate polymer	4

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	Sodium carbonate	5
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Perfume Delivery System (Example I)	4.0
	Suds suppressor	2
5	Enzymes*	1.5
	Soil release agent	0.2
	Minors, filler** and water	Balance to 100%

\*1:1:1 mixture of protease, lipase, and cellulase.

\*\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, 10 clay, silicates, and the like.

An aqueous crutcher mix of heat and alkali stable components of the detergent composition is prepared and spray-dried. The other ingredients, including the perfume delivery system, are admixed therewith so that the final composition contains the 15 ingredients tabulated at the levels shown.

The detergent granules are added via the dispensing drawer together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine. Actual weight of detergent composition is taken to provide an 8,000 ppm concentration in the 17 l water-20 fill machine. Fabrics laundered with the composition and line-dried have a noticeable perfume fragrance after either ironing or storage.

#### EXAMPLE IV

A laundry bar comprises the following.

	<u>Component</u>	<u>Weight %</u>
25	C <sub>12</sub> linear alkyl benzene sulfonate	30
	Phosphate (as sodium tripolyphosphate)	7
	Sodium carbonate	25
	Sodium pyrophosphate	7
30	Coconut monoethanolamide	2
	Zeolite A (0.1-10 micron)	5
	Carboxymethylcellulose	0.2
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Polyacrylate (m.w. 1400)	0.2
35	Nonanoyloxybenzenesulfonate	5
	Sodium percarbonate*	5

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	Brightener	0.2
	Perfume delivery system (Example I)	3.0
	Protease	0.3
	CaSO <sub>4</sub>	1
5	MgSO <sub>4</sub>	1
	Water	4
	Filler**	Balance to 100%

\*Average particle size of 400 to 1200 microns.

\*\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc,  
10 clay, silicates, and the like.

The detergent laundry bar is extruded in conventional soap or  
detergent bar making equipment as commonly used in the art.  
Testing is conducted following the testing methods in Example II.  
Fabrics laundered with the composition and line-dried have a  
15 noticeable perfume fragrance after ironing or storage.

#### EXAMPLE V

A high density granular detergent comprises the following.

	<u>Component</u>	<u>Weight %</u>
	C <sub>12</sub> -14 linear alkyl benzene sulfonate	15
20	Sodium citrate	5
	Sodium carbonate	20
	Zeolite A (0.1-10 micron)	26
	Brightener	0.1
	Perfume delivery system (Example I)	3.0
25	Detergent enzyme (1:1 LIPOLASE/ESPERASE)	1.0
	Sodium Sulphate	15
	Water and fillers**	Balance to 100%

\*\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc,  
clay, silicates, and the like.

30 An aqueous crutcher mix of heat and alkali stable components  
of the detergent composition is prepared and spray-dried. The  
resulting granules are passed through a Lodige CB mixer until a  
density of 650 grams/liter is secured. The other ingredients,  
including the perfume delivery system, are admixed therewith so  
35 that the final composition contains the ingredients tabulated at  
the levels shown.

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Testing is conducted following the testing methods in Example II. Fabrics laundered with the composition have a noticeable perfume fragrance after drying in an automatic dryer at 60-70°C for approximately 40 minutes.

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What is Claimed is:

1. A perfume delivery composition in the form of particles comprising:
  - a) a solid, water-insoluble, porous carrier which comprises a natural or synthetic zeolite having a nominal pore size of at least 6 Angstroms;
  - b) a perfume which is releasably incorporated in the pores of said zeolite carrier to provide a perfumed zeolite; and
  - c) a matrix coated on said perfumed zeolite which comprises a water-soluble composition in which the perfume is substantially insoluble, comprising from 0% to 80%, by weight, of at least one solid polyol containing more than 3 hydroxyl moieties and from 20% to 100%, by weight, of a fluid diol or polyol in which the perfume is substantially insoluble and in which the solid polyol is substantially soluble.
2. A composition according to Claim 1 wherein said fluid polyol or diol is selected from the group consisting of glycerol, ethylene glycol, and diglycerol.
3. A composition according to either of Claims 1 or 2 wherein the solid polyol is selected from the group consisting of glucose, sorbitol, maltose, glucamine, sucrose, polyvinyl alcohol, starch, alkyl polyglycoside, sorbitan fatty ester, polyhydroxy fatty acid amides whose fatty acid moieties contain from 1 to 18 carbon atoms, and mixtures thereof.
4. A composition according to any of Claims 1-3 wherein the zeolite is Zeolite X or Zeolite Y.
5. A composition according to any of Claims 1-4 wherein the perfume is selected from the group consisting of hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.
6. A composition according to any of Claims 1-5 wherein the perfumed zeolite comprises from 5% to 30%, by weight, of the perfume.
7. A composition according to any of Claims 1-6 wherein the perfume further comprises a perfume fixative.

8. A granular detergent composition comprising:
  - a) from 5% to 80%, by weight, of a detergents surfactant; and
  - b) from 1% to 20%, by weight, of the perfume delivery composition according to any of Claims 1-7.
9. A detergent composition according to any of Claims 1-8 further comprising a second perfume sprayed onto the surface of said detergent granules.
10. A perfume delivery composition derived by a process which comprises the steps of:
  - (a) forming a perfumed zeolite by mixing porous, substantially dehydrated Zeolite X or Y with a perfume such that the perfume is incorporated into the pores of the zeolite;
  - (b) forming a matrix by mixing a solid polyol containing more than 3 hydroxyl moieties with glycerol, ethylene glycol, or diglycerol to form a liquid; and
  - (c) mixing the matrix (b) with the perfumed zeolite (a) until free flowing particles are formed.

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 5 C11D3/50 C11D17/00 C11D3/12 A61K7/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 5 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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**PCT**WELTOORGANISATION FÜR GEISTIGES EIGENTUM  
Internationales BüroINTERNATIONALE ANMELDUNG VERÖFFENTLICH NACH DEM VERTRAG ÜBER DIE  
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

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(30) Prioritätsdaten: 3037/95 27. Oktober 1995 (27.10.95) CH 2518/96 15. Oktober 1996 (15.10.96) CH		Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>	
(71) Anmelder ( <i>für alle Bestimmungstaaten außer US</i> ): GIVAUDAN-ROURE (INTERNATIONAL) S.A. (CH/CH); Chemin de la Parfumerie 5, CH-1214 Vernier (CH).		<i>W/Equivalent</i> <i>US 6,056,949</i>	
(72) Erfinder; und (75) Erfinder/Anmelder ( <i>nur für US</i> ): MENZI, Heini (CH/CH); Grünenhofstrasse 6, CH-8625 Gossau (CH). PER- REN, Matthias (CH/CH); Fröhlichstrasse 40, CH-5200 Brugg (CH). RINGGENBERG, Rudolf (CH/CH); Rümelbachstrasse 17, CH-8153 Rümlang (CH).			
(74) Gemeinsamer Vertreter: GIVAUDAN-ROURE (INTERNA- TIONAL) S.A.; Patentdienst, Postfach 3255, CH-4002 Basel (CH).			

(54) Title: AROMATIC GRANULATED MATERIAL

(54) Bezeichnung: AROMENGRANULAT

(57) Abstract

The present invention relates to a process for the preparation of spherical, or substantially spherical, practically dust-free aromatic and odoriferous granulated material which is free-flowing, mechanically stable and has a narrow grain-size distribution.

(57) Zusammenfassung

Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung von sphärischen bzw. im wesentlichen sphärischen, praktisch staubfreien, freifließenden, mechanisch stabilen Aromen- und Riechstoffgranulaten mit enger Korngrößenverteilung.

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### Aromengranulat

- Die vorliegende Erfindung betrifft ein Verfahren zur Herstellung von sphärischen bzw. im wesentlichen sphärischen, praktisch staubfreien, freifließenden, mechanisch stabilen Aromen- und Riechstoffgranulaten
- 5 mit enger Korngrößenverteilung.

Unter "sphärisch" wird im vorliegenden Fall ein bei visueller Betrachtung, mit unbewaffnetem Auge, kugelförmiges, bzw. ein im wesentlichen kugelförmiges Material verstanden.

- Aromengranulate sind bekannt. EP 0070719 beschreibt die Herstellung
- 10 von Aromengranulaten, die in einem konventionellen Fliessbett, gebildet durch reine Aufwirbelung von Luft, hergestellt werden. Diese Produkte weisen jedoch die Nachteile einer ungenügenden mechanischen Festigkeit, des relativ grossen Staubanteils und einer beschränkten Fliessfähigkeit auf.

- Ziel der vorliegenden Erfindung war ein Verfahren, das erlaubt,
- 15 Produkte herzustellen, die die geschilderten Nachteile nicht mehr aufweisen, und dementsprechend bei ihrer Verwendung, also bei der Einarbeitung in das zu aromatisierende bzw. parfümierende Material, eindeutig bevorzugt werden. Im Vordergrund stehen Nahrungsmittel, Genussmittel und Getränke, Pharmazeutika, kosmetische Produkte,
- 20 Hygieneprodukte, z.B. Mundhygieneprodukte, Windeln, Seifen, Detergentien, Haushaltprodukte, etc.

Zusätzlich können die erfindungsgemäss erhältlichen Aromen- und Riechstoffgranulate in einem zweiten Schritt auf einfache Weise mit einer Umhüllung versehen werden, ohne dass der nun erfindungsgemäss verwendete Rotorgranulator ausgeschaltet oder umgerüstet, oder Produkt 5 transferiert werden muss. Die Umhüllung bezweckt auch eine verbesserte Einkapselung der Wirkstoffe, eine Aenderung, d.h. Verbesserung des Löslichkeitsverhaltens oder eine gezielte Schutzwirkung zu erreichen.

Rotorgranulatoren wurden bis anhin in der Produktion von Waschmittelzusätzen, Düngemitteln und Pharmawirkstoffen eingesetzt (siehe z.B. 10 den Firmenprospekt GRCG Typ 1-200 der Firma Glatt, Pratteln, Schweiz Juni 1992]).

Die Apparatur besteht im wesentlichen aus einer Fliessbetteinrichtung und der Zu- und Ablufteinheit. Zweckmässig ist z.B. ein zylindrischer Behälter mit vertikaler Drehachse, dessen Boden um die Zentralachse 15 rotiert. Der Zylindermantel ist zweckmässigerweise feststehend. Die Drehzahl beträgt zweckmässigerweise ca. 50-500/min. Das im Prozess vorgelegte Kernmaterial wird mittels einer rotierenden Bodenplatte in Bewegung gesetzt. Durch den (peripheren) Ringspalt zwischen rotierender Bodenplatte und feststehender Behälterwand strömt eine relativ geringe 20 Menge Luft, die zusammen mit der Rotationsbewegung der Bodenplatte das vorgelegte Gut in Bewegung versetzt, "fluidisiert". Im Vergleich zu früheren Technologien, die die nötige Bewegung des Gutes nur mit Hilfe der Luft erzeugten, wird nur ca. 1/5 - ca. 1/3 der Luft benötigt, um den vorgelegten Feststoff zu fluidisieren, zu bewegen.

25 Das neue Verfahren ist dadurch gekennzeichnet, dass in ein in einem Fliessbett-Rotorgranulator fluidisierten Kernmaterial eine Aroma- oder Riechstoffemulsion submers - in das Fliessbett - eingesprüh und so granuliert wird. Das Verfahren beinhaltet also im wesentlichen die Verwendung eines Fliessbett-rotorgranulators bei der Herstellung von 30 sphärischen Aromen- und Riechstoffgranulaten.

Gegen die Verwendung solcher Apparaturen für Aromen- bzw. Riechstoffkompositionen sprach der doch immer noch relativ hohe Luftdurchsatz und die doch relativ lange Reaktionszeit - dies im Hinblick auf zu befürchtende Verluste an - insbesondere - leicht flüchtigen 35 Komponenten.

- Das Kernmaterial ist ein für die Herstellung von Aromen- oder Riechstoffgranulat üblicherweise verwendeter, in der Industrie zugelassener oder pharmazeutisch anwendbarer Feststoff, zweckmässigerweise mit Korngrössen von ca. 0,02 bis ca. 3,0 mm, insbesondere von 0,2 bis ca. 1,5 mm
- 5 Durchmesser. Es ist beispielsweise ein Kohlenhydrat, z.B. ein Zucker, wie Glucose, Lactose, Saccharose, oder auch ein Produkt komplexerer Zusammensetzung, wie Fruchtpulver, z.B. Orangensaftpulver, oder Gemüsepulver, z.B. Karottensaftpulver, oder ein Zuckeralkohol, wie Isomalt, oder Pectin, hydrolysiertes Pflanzenprotein (HVP), Nahrungsfasern, z.B. Trester, Weizenfasern, Cellulosefasern, etc., oder ein organisches oder anorganisches Salz, z.B. ein Citronensäuresalz oder Kochsalz, aber auch Kräuterpulver, Gewürzpulver, Teepulver kommen in Frage.

- Das Trägermaterial für die eingesprühte Emulsion wird generell aus 15 für diese Zwecke üblichen Materialien ausgewählt, es ist zweckmässigerweise ein Kohlenhydrat, z.B. chemisch modifizierte Stärke, abgebaute Stärke (Dextrin, Maltodextrin); natürliche Harze, Exudate, z.B. Gummi arabicum, Pflanzenextrakte, wie Carragenan, Alginate, etc. ein Protein, z.B. ein Milchprotein, oder Gelatine, etc. oder eine Kombination solcher 20 Stoffe.

Als Lösungsmittel für die Emulsion können beispielsweise Wasser oder Wasser/Ethanolgemische dienen.

- Bei der Granulierung können auch übliche Zusatzstoffe, wie künstliche Süsstoffe, Lebensmittelfarbstoffe, Vitamine, Antioxidantien, Antischaummittel, Kohlensäuregeneratoren wie Weinsäure, Genusssäuren wie 25 Citronensäure, oder zusätzliche Geschmackstoffe, etc. verwendet werden, die dem Kernmaterial oder der Sprühemulsion zugesetzt werden können.

- Nach der Granulierung kann eine Umhüllung der Partikel erfolgen, z.B. durch Aufsprühen, z.B. einer Lösung, Emulsion oder Schmelze einer 30 für diese Zwecke bekanntmassen geeigneten, eine Schutzhaut bzw. einen Film bildenden Substanz bzw. eines Substanzgemisches, wie z.B. Fett, oder modifizierte Cellulose, Gelatine, Pflanzen- oder Tierextrakte, Exudate, z.B. Gummi arabicum, abgebaute Stärke oder chemisch modifizierte Stärke, pharmazeutisch anwendbare Kunststoffe, z.B. Polyvinylpyrrolidon, 35 Polyäthylenglykol, etc.

Die geeigneten Lufttemperaturen sind erhöhte Temperaturen, z.B. ca. 30°, bzw. 40° - ca. 80°C, bevorzugt ca. 40°, bzw. 50 - ca. 70°C.

- Es kommen alle gängigen Aromen und Riechstoffe in Frage, also z.B. Richtung Fleisch, Käse, Frucht, z.B. Citrus, Beeren, Tabak, Blumen, Holz,
- 5 Gewürz, Ambra, etc., die in der Industrie Verwendung finden können. Als Aromen- und Riechstoffkomponenten kommen alle die bisher für Aromen und Riechstoffe(granulate) üblicherweise verwendeten Komponenten in Frage, also einzelne solche Komponenten, z.B. Menthol oder Vanillin, etc. - oder aber ätherische Oele oder Fraktionen oder Gemische von Aroma- und
  - 10 Riechstoffkompositionen. Die einzelnen Komponenten können natürlichen (pflanzlichen oder tierischen) oder synthetischen Ursprungs sein.

Die enge Korngrößenverteilung wird im wesentlichen erzielt durch das Zusammenwirken der Parameter: Korngröße des Trägermaterials, Zusammensetzung der Emulsion, Sprührate der Emulsion (ca. 30 - ca.

- 15 80 g/min., [z.B. im Falle der Apparatur des Beispiels 1] bzw. 3-8 g/min\*kg (Gesamtansatz), Struktur der rotierenden Bodenplatte - z.B. glatt, genoppt oder geriffelt, Drehzahl der rotierenden Bodenplatte, Zuluftgeschwindigkeit, Lufttemperatur (ca. 20 - ca. 80°C). Diese Beeinflussung durch die Art und Weise der Granulierung ist dem Fachmann bekannt und die enge
- 20 Verteilung kann durch Versuche ermittelt werden. Wie eingangs erwähnt, führt sie im Falle des vorliegenden Verfahrens zu besonders günstigen Werten.

Unter "einem im wesentlichen staubfreien Produkt" wird im vorliegenden Fall ein Granulat verstanden, das einen Feinanteil (im wesentlichen Kernmaterial und Trägermaterial) aufweist, der unter 5% liegt, dies bei Partikelgrößen von <0,1 mm.

Ein erfindungsgemäss erhältliches, im wesentlichen sphärisches Granulat ist in der Figur 1 abgebildet.

#### Beispiel 1: Zitronengranulat

- 30 Im Rotorgranulator (Typ GPCG-5, Firma Glatt, Pratteln) werden 2,975 kg Griesszucker und 2,975 kg Puderzucker vorgelegt.

In einem separaten Behälter werden 800 g Wasser bei Raumtemperatur vorgelegt, danach werden 595 g Maltodextrin und 105 g chemisch modifizierte Stärke (Dextrin) zugegeben und darin gelöst. Unter starkem

- Röhren (18500 UpM) mit einer Mischturbine vom Typ Polytron der Firma Kinematika, Littau werden 350 g Zitronenaroma (praktisch ausschliesslich Zitronenöl) langsam zugegeben. Es wird noch 3 Minuten weiter homogenisiert, bis eine stabile Sprühemulsion entsteht. Der Rotorgranulator wird in  
5 Betrieb gesetzt und die Sprühemulsion (70 g/min.) über eine Zweistoffdüse (Emulsion/Druckluft) submers, ca. auf der halben Höhe des Fliessbetts zugepumpt. Wenn die Sprühemulsion aufgebraucht ist, wird das Aromengranulat noch während 5-10 Minuten nachgetrocknet. Dadurch entsteht ein freifliessendes Aromengranulat mit einer Korngrössenverteilung von 87%  
10 innerhalb 0,2-1,6 mm und einem Schüttgewicht von 0,65 g/ml.

Beispiel 2: Limettegranulat

Als Kernmaterial werden 4,662 kg Isomalt vorgelegt.

- Die Sprühemulsion wird wie im Beispiel 1 hergestellt und besteht aus 2 l Wasser, 1,260 kg Gummi arabicum, 26,6 g Tartrazin (gelber Farbstoff),  
15 1,4 g Indigotin (blauer Farbstoff) und 1,050 kg Limettenaroma (praktisch ausschliesslich Limettenöl). Das Kernmaterial wird in Bewegung versetzt (350 U/min.) bzw. fluidisiert und die Sprühemulsion mit 75 g/min. eingesprüht. Es entsteht ein Aromengranulat mit 87% der Partikeln zwischen 0,2 und 0,8 mm und einem Schüttgewicht von 0,71 g/ml.

Beispiel 3: Gewürzgranulat

Die Vorlage setzt sich aus 1,680 kg Kochsalz, 1,680 kg Kristallzucker und 2,380 kg HVP-Pulver (hydrolysiertes Pflanzenprotein) zusammen.

- Wie im Beispiel 1 wird die Sprühemulsion hergestellt, welche 1 l Wasser, 679,7 g Maltodextrin, 210 g modifizierte Stärke und 370,3 g einer Gewürz-Aromenkomposition (basierend auf Zitronengrasöl + Pfefferoleoresin) enthält. Durch das Starten des Rotorgranulators (300 U/min.) wird die Vorlage gemischt und in Bewegung versetzt. Die Sprühemulsion wird eingesprüht (30 g/min.). Sobald fertig granuliert und getrocknet ist, werden 350 g eines geschmolzenen Pflanzenfettes mit einer Temperatur von  
25 50-60°C eingesprüht. Die Temperatur im Granulator ist zu diesem Zeitpunkt unter 40°C, womit das Fett auf der Granulatoberfläche erstarrt. Dadurch wird ein umhülltes Granulat mit Gewürzgeschmack erhalten.  
30

Beispiel 4: Fruchtaroma

- In diesem Fall werden 2,450 kg Griesszucker und 3,500 kg eines Multivitaminpräparates (Hoffmann-La Roche, Basel) im Rotorgranulator vorgelegt. Die Sprühemulsion setzt sich aus 1 l Wasser, 595 g Maltodextrin, 105 g 5 modifizierter Stärke und 350 g Fruchtaroma zusammen und wird analog zum Beispiel 1 hergestellt. Der Granulator wird wie im Beispiel 1 betrieben, die Sprühemulsion zu 50 g/min. zudosiert.

Beispiel 5: Parfümiertes Granulat

Im Rotorgranulator werden 5,250 kg Maltodextrin vorgelegt.

- 10 Die Sprühemulsion wird wie in den Beispielen 1 bis 4 hergestellt. Sie besteht aus 1,500 kg Wasser, 0,875 kg Maltodextrin, 0,175 g chemisch modifizierter Stärke und 0,700 kg eines beliebigen Riechstoffgemisches für Parfümeriezwecke.

- Das Kernmaterial wird in Bewegung versetzt (400 U/min.) bzw. 15 fluidisiert und die Sprühemulsion mit 85 g/min. eingespritzt. Es entsteht ein Parfümeriegranulat, das mit 0,350 kg Polyglykol 6000S, gelöst in 0,350 kg Ethanol, und 0,175 kg Wasser umhüllt wird. Das Wasser und das Ethanol verdampfen und das Polyglykol bildet einen Film um das Riechstoff- granulat.
- 20 Die im Rahmen der vorliegenden Erfindung angegebenen Apparateparameter beziehen sich immer auf den für den Laborbetrieb geeigneten Rotorgranulator GPCG-5 mit einem Durchmesser von 50 cm und einer Höhe von 1,9 m (Fließbett 92 cm); für den Fall anderer Apparatedimensionen sind Abweichungen möglich.
- 25 Die in den Beispielen 1 bis 5 erwähnten Aromen- und Riechstoffgranulate werden in den zu aromatisierenden Lebensmitteln, wie z.B. Teepulver, Kräutermischungen, Kaugummi, gefrorenen Fertigmenues, Weich- und Hartbonbons, Biskuit, Eiscrème, Eiscremecoating, Schokoladeriegel, Constant-Getränkepulvern, Suppen- und Saucenbeuteln, 30 Mundhygieneprodukten, wie Gebissreinigungstabletten und Zahnpasten, etc. eingesetzt oder in den zu parfümierenden Kosmetik-, Hygiene-, Pharma-, Seifen-, Detergenzien- oder Haushaltprodukten verwendet.

Beispiel 6: Applikationen für die erfindungsgemässen GranulateTeebeutel

Zu gebrochenen Teeblättern wird 2-12% granulierte Aroma, z.B. Limette, gemischt und in Teebeutel verpackt.

- 5 Die Vorteile gegenüber konventionellen Pulveraromen sind die folgenden:

- Das Granulat dringt aufgrund der Partikelgrösse nicht durch die Papierporen => kein Verlust bei Transport und Lagerung.
- Kein Abrieb der Granulatpartikel bei Verarbeitung und Transport, da 10 mechanisch resistent.
- Das Aroma löst sich rasch und vollständig auf, wenn der Teebeutel in heisses Wasser getaucht wird.

Instant Getränkypulver

Zu einem Instant Getränkypulver auf Zuckerbasis wird 1-2% eines 15 granulierten Aromas, z.B. Tropenfrucht-Mix, gemischt.

- Die Vorteile gegenüber konventionellen Pulveraromen sind insbesondere:

- Keine Entmischung bei Abpackung und Transport, da die Granulatpartikelgrösse auf die Partikelgrösse des Getränkypulvers abgestimmt wird.
- Verbesserte Lagerstabilität der erfindungsgemässen Citrusaromen.
- Schnelle Auflösung des Aromas, wenn das Getränkypulver in kaltem Wasser gerührt wird.

Kaugummi

Ein orange-gefärbtes granuliertes Aroma, z.B. Pfirsich wird zu 0,5% in 25 eine Kaugummimasse eingearbeitet, die bereits ein flüssiges Aroma, z.B. Zitrone enthält.

Der Kaugummi weist dadurch die folgenden Vorteile auf, die mit konventionellen Pulveraromen nicht erreicht werden können:

- attraktive, gut sichtbare Partikel, die während der Lagerung stabil bleiben.
  - ein doppelter Aroma-Effekt, wobei die beiden Aromen separat wahrgenommen werden.
- 5 - ein sehr rasches Wahrnehmen des granulierten Aromas nach wenigen Sekunden Kauens, gefolgt vom flüssigen Aroma. Bei jedem Biss auf ein Granulat-Korn wird Aroma wieder neu freigesetzt.

#### Hart- und Kaubonbons

- Ein braun gefärbtes granulierte Aroma, z.B. Zimt, wird zu 0,2-0,4% in
- 10 eine Hart- oder Kaubonbonmasse eingemischt, die mit einem flüssigen Aroma, z.B. Apfel aromatisiert ist.

Vorteile:

- attraktive, sichtbare Partikel, die während der Lagerung stabil bleiben.
- ein doppelter Aroma-Effekt, wobei die beiden Aromen separat wahrgenommen werden. In diesem Fall entsteht der Eindruck von Apfelstrudel.

#### Schokolade

Ein Cola-Aroma, das Na-bicarbonat und Zitronensäure enthält, wird zu 1-4% in eine Schokoladenmasse eingearbeitet.

Vorteil:

- 20 Beim Essen entwickelt sich sofort ein prickelnder Effekt, indem sich unter dem Einfluss der Speichelfeuchtigkeit Kohlensäure bildet.

#### Icecream mit Schokoladeüberzug

- In die Schokolademasse wird 1-3% eines granulierten Fruchtaromas, z.B. Zitrone, das auch Zitronensäure enthält, eingemischt. Die Schokolade
- 25 wird auf die übliche Art als dünner Ueberzug auf das fertige Icecream aufgetragen.

Beim Konsumieren des Icecreams machen sich folgende Vorteile bemerkbar:

- 9 -

- Oertlich definierter fruchtiger Geschmack, wie von Fruchtpartikeln, in der Schokolade.
  - Der Fruchteindruck wird verstrkt durch die Zitronensure, was mit ublichen Pulveraromen nicht mglich ist.
- 5 5 - Granulierte Aromen mit einer Partikelgresse von 0,8-2 mm ergeben  
zustzlich einen knusprigen Effekt beim Daraufbeissen.

#### Gefrorenes Reisgericht

- Ein Wrzaroma, das Salz enthlt und zustzlich mit einer Hartfett-  
schicht berzogen ist (Beispiel 3), wird zum gekochten, abgekhlten Reis  
10 gemischt oder aufgestreut.

Vorteil:

Da das Salz in den Partikeln eingeschlossen ist, lst es sich nicht auf  
und verursacht keine Aenderung des Gefrierverhaltens des Reisgerichtes.

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Legende

- 1) Teilchenstruktur
- 2) Nukleus, Kern  
(Trägermaterial, hauptsächlich Kohlehydrate)
- 5 3) enkapsuliertes Aroma  
(Aroma ist im filmbildenden Agens eingeschlossen)
- 4) Umhüllung, Hülle  
(fakultativ, z.B. aus Fett, Protein, Kohlehydraten oder Gemischen davon)

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Patentansprüche

1. Verfahren zur Herstellung von sphärischem Granulat, dadurch gekennzeichnet, dass in ein in einem Fliessbett-rotorgranulator fluidisiertes Kernmaterial eine Aroma- bzw. Riechstoffemulsion submers eingesprührt und auf diese Weise granuliert wird.
2. Verfahren nach Anspruch 1, worin das Kernmaterial ein in der Lebensmittel-, der kosmetischen, pharmazeutischen oder Konsumgüter-industrie zugelassener Feststoff ist und zweckmässigerweise Korngrössen von ca. 0,02 bis ca. 3,0 mm aufweist.
- 10 3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass das Kernmaterial ein Kohlenhydrat, z.B. ein Zucker wie Glucose, Lactose, Saccharose, Stärke oder abgebaute Stärke, oder ein Zuckeralkohol wie Isomalt, oder Pectin, hydrolysiertes Pflanzenprotein, Nahrungsfasern, organische oder anorganische Salze darstellt.
- 15 4. Verfahren nach Anspruch 1, 2 oder 3, worin das Trägermaterial für die Sprühemulsion chemisch modifizierte Stärke, abgebaute Stärke, wie z.B. Maltodextrine, natürliche Harze, Exudate wie z.B. Gummi arabicum, Gelatine oder Pflanzenextrakte wie z.B. Carragenan oder Alginate, in Wasser oder Wasser/Akkohol-Gemischen ist.
- 20 5. Verfahren nach Anspruch 1 bis 4, worin bei der Herstellung der Sprühemulsion eine individuelle Aromen- oder Riechstoffkomponente oder ein Gemisch von verschiedenen Komponenten natürlicher oder synthetischer Herkunft eingesetzt wird.
- 25 6. Verfahren nach Anspruch 1 bis 5, worin der Aromen- oder Riechstoffanteil ca. 1 bis ca. 25%, insbesondere ca. 5 bis ca. 15%, vorzugsweise ca. ≤10%, des fertigen Aromen- oder Riechstoffgranulates ausmacht und der Rest im wesentlichen aus Kernmaterial und Trägermaterial besteht.
- 30 7. Verfahren nach Anspruch 1 bis 6, worin die an der Erzeugung des Fliessbetts mitbeteiligte Luft auf ca. 20 bis ca. 80°C, insbesondere auf ca. 40 bis ca. 60°C, erwärmt wird.
8. Verfahren nach Anspruch 1 bis 7, worin ein Aromen- oder Riechstoffgranulat mit einer Partikelgrösse im Bereich von ca. 0.05 bis ca. 3,0, vorzugsweise im Bereich von ca. 0,2 bis ca. 1,5 mm hergestellt wird.

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9. Verfahren nach Anspruch 1 bis 8, worin ein Produkt hergestellt wird, das zu  $\geq 95\%$  aus Partikeln von ca. 0,2 - ca. 3 mm Durchmesser, bzw. zu ca. 80% aus Partikeln, die eine Bandbreite von nur ca. 0,6 mm aufweisen, besteht.
- 5      10. Verfahren nach Anspruch 1 bis 9, worin nach der Granulierung eine Umhüllung der Partikel, erfolgt, und zwar durch submerses Aufsprühen einer Lösung, Emulsion oder Schmelze einer Substanz bzw. eines Substanzgemisches, wie z.B. Fett, oder modifizierter Cellulose, Gelatine, Pflanzen- oder Tierextrakten, Exudaten wie Pflanzengummi, 10 abgebaute Stärke oder chemisch modifizierte Stärke, pharmazeutisch anwendbaren Kunststoffen, etc.
11. Verfahren nach Anspruch 1 bis 10, worin bei der Granulierung Zusatzstoffe wie künstliche Süßstoffe, Lebensmittelfarbstoffe, Vitamine, Antioxidantien, Antischäummittel, Kohlensäuregeneratoren, Genuss- 15 säuren verwendet werden, die als solche dem Kernmaterial oder der Sprühemulsion zugesetzt werden.
12. Verwendung eines Fliessbett-rotorgranulators bei der Herstellung von sphärischem Aromen- oder Riechstoffgranulat.
13. Verwendung eines gemäss Verfahren einer der Ansprüche 1 bis 11 20 hergestellten Aromen- oder Riechstoffgranulats zu Aromatisierungs- oder Parfümierungszwecken.
14. Verfahren zur Herstellung von sphärischem Aromengranulat gemäss Anspruch 1, dadurch gekennzeichnet, dass in ein in einem Fliess- 25bett-rotorgranulator fluidisiertes Kernmaterial eine Aromaemulsion submers eingesprüht und auf diese Weise granuliert wird.
15. Verfahren nach Anspruch 14, worin das Kernmaterial ein in der Lebensmittelindustrie zugelassener Feststoff ist und zweckmässigerweise Korngrössen von ca. 0,02 bis ca. 3,0 mm aufweist.
16. Verfahren nach Anspruch 14 oder 15, dadurch gekennzeichnet, 30 dass das Kernmaterial ein Kohlenhydrat, z.B. ein Zucker wie Glucose, Lactose, Saccharose, oder ein Zuckeralkohol wie Isomalt, oder Pectin, hydrolysiertes Pflanzenprotein, Nahrungsfasern, organische oder anorganische Salze darstellt.

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17. Verfahren nach Anspruch 14, 15 oder 16, worin das Trägermaterial für die Sprühemulsion chemisch modifizierte Stärke, abgebaute Stärke, wie z.B. Maltodextrinen, natürliche Harze, Exudate wie z.B. Gummi arabicum, Gelatine oder Pflanzenextrakte wie z.B. Carragenan oder Alginaten, in  
5 Wasser oder Wasser/Alkohol-Gemischen ist.
18. Verfahren nach Anspruch 14 bis 17, worin bei der Herstellung der Sprühemulsion eine individuelle Aromenkomponente oder ein Gemisch von verschiedenen Komponenten natürlicher oder synthetischer Herkunft eingesetzt wird.
- 10 19. Verfahren nach Anspruch 14 bis 18, worin der Aromenanteil ca. 1 bis ca. 25%, insbesondere ca. 5 bis ca. 15% des fertigen Aromengranulates ausmacht und der Rest im wesentlichen aus Kernmaterial und Trägermaterial besteht.
- 15 20. Verfahren nach Anspruch 14 bis 19, worin die an der Erzeugung des Fliessbetts mitbeteiligte Luft auf ca. 20 bis ca. 80°C, insbesondere auf ca. 40 bis ca. 60°C, erwärmt wird.
21. Verfahren nach Anspruch 14 bis 20, worin ein Aromengranulat mit einer Partikelgrösse im Bereich von ca. 0,05 bis ca. 3,0, vorzugsweise im Bereich von ca. 0,2 bis ca. 1,5 mm hergestellt wird.
- 20 22. Verfahren nach Anspruch 14 bis 21, worin ein Produkt hergestellt wird, das zu >95% aus Partikeln von ca. 0,2 - ca. 3 mm Durchmesser, bzw. zu ca. 80% aus Partikeln, die eine Bandbreite von nur ca. 0,6 mm aufweisen, besteht.
- 25 23. Verfahren nach Anspruch 14 bis 22, worin nach der Granulierung eine Umhüllung der Partikel, erfolgt, und zwar durch Aufsprühen einer Lösung, Emulsion oder Schmelze einer Substanz bzw. eines Substanzgemisches, wie z.B. Fett, oder modifizierter Cellulose, Gelatine, Pflanzen- oder Tierextrakten, Exudaten wie Pflanzengummi, abgebaute Stärke oder chemisch modifizierte Stärke, pharmazeutisch anwendbaren Kunststoffen,  
30 etc.
24. Verfahren nach Anspruch 14 bis 23, worin bei der Granulierung Zusatzstoffe wie künstliche Süsstoffe, Lebensmittelfarbstoffe, Vitamine, Antioxidantien, Antischäummittel, Kohlensäuregeneratoren, Genuss-

- 14 -

säuren verwendet werden, die als solche dem Kernmaterial oder der Sprühemulsion zugesetzt werden.

25. Verwendung eines Fliessbett-rotorgranulators bei der Herstellung von sphärischem Aromengranulat.

5 26. Verwendung eines gemäss Verfahren einer der Ansprüche 14 bis 24 hergestellten Aromengranulats zu Aromatisierungszwecken.

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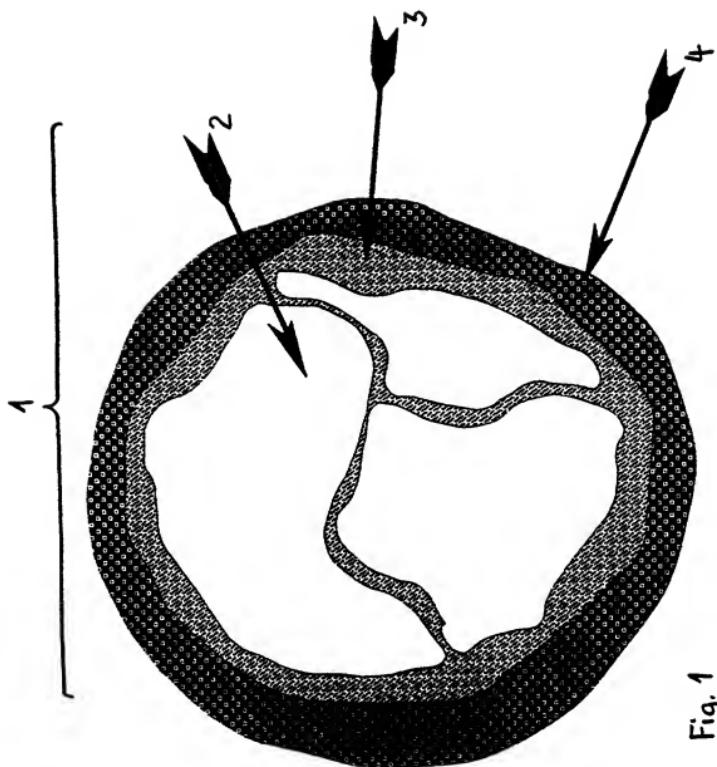


Fig. 1

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/CH 96/00373

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 A23L1/22 A23P1/02 A61K7/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 A23L A23P A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 070 719 A (UNILEVER) 26 January 1983 cited in the application see claims; examples ---	1,3,5, 14,16,26
A	EP 0 011 324 A (PROCTER & GAMBLE) 28 May 1980 see claims ---	1-26
A	WO 91 09989 A (DANSK TYGGEGLUMMI FABRIK) 11 July 1991 see claims ---	1
A	WO 95 15821 A (WM.WRIGLEY JR.) 15 June 1995 see claims ---	1,14
A,P	WO 96 23423 A (NESTLE) 8 August 1996 see claims -----	1,14

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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\*Z\* document member of the same patent family

1 Date of the actual completion of the international search

Date of mailing of the international search report

26 March 1997

07. 04. 97

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Van Moer, A

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CH 96/00373

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 70719 A	26-01-83	AU 558654 B AU 8612182 A BR 8204214 A CA 1190477 A JP 1584973 C JP 2001528 B JP 58024336 A US 4576737 A	05-02-87 27-01-83 12-07-83 16-07-85 31-10-90 11-01-90 14-02-83 18-03-86
EP 11324 A	28-05-88	CA 1145191 A JP 55104874 A	26-04-83 11-08-80
WO 9109989 A	11-07-91	AU 7051391 A CA 2070288 A DE 69007124 D EP 0506793 A JP 5504057 T	24-07-91 22-06-91 07-04-94 07-10-92 01-07-93
WO 9515821 A	15-06-95	US 5447565 A AU 1303795 A	05-09-95 27-06-95
WO 9623423 A	08-08-96	US 5496574 A US 5580593 A AU 4715396 A	05-03-96 03-12-96 21-08-96

## INTERNATIONALER RECHERCHENBERICHT

internationales Aktenzeichen  
PCT/CH 96/00373

A. KLASIFIZIERUNG DES ANMELDUNGSGEGENSTANDES  
IPK 6 A23L1/22 A23P1/02 A61K7/46

Nach der internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK:

## B. RECHERCHIERTE GEBIETE

Recherchierte Mindestprästoff (Klassifikationssystem und Klassifikationsymbole)  
IPK 6 A23L A23P A61K

Recherchierte aber nicht zum Mindestprästoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

## C. ALS WESENTLICH ANGEGEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	EP 0 070 719 A (UNILEVER) 26.Januar 1983 in der Anmeldung erwähnt siehe Ansprüche; Beispiele ---	1,3,5, 14,16,26
A	EP 0 011 324 A (PROCTER & GAMBLE) 28.Mai 1980 siehe Ansprüche ---	1-26
A	WO 91 09989 A (DANSK TYGGEGUMMI FABRIK) 11.Juli 1991 siehe Ansprüche ---	1
A	WO 95 15821 A (WM.WRIGLEY JR.) 15.Juni 1995 siehe Ansprüche ---	1,14
A,P	WO 96 23423 A (NESTLE) 8.August 1996 siehe Ansprüche -----	1,14

Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

Siehe Anhang Patentsammlung

- \* Besondere Kategorien von angegebenen Veröffentlichungen :
- \*'A' Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist
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\*'Y' Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist

\*'g' Veröffentlichung, die Mitglied derselben Patentsammlung ist

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Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
26.März 1997	07. 04. 97
Name und Postanschrift der internationale Recherchenbehörde Europäisches Patentamt, P.B. 5818 Patentanlagen 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl. Fax (+ 31-70) 340-3016	Befolmächtigter Bediensteter  Van Moer, A

## INTERNATIONALER RECHERCHENBERICHT

Angaben zu Veröffentlichungen, die zur selben Patentfamilie gehören

Int. nationales Aktenzeichen

PCT/CH 96/00373

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP 70719 A	26-01-83	AU 558654 B AU 8612182 A BR 8204214 A CA 1190477 A JP 1584973 C JP 2001528 B JP 58024336 A US 4576737 A	05-02-87 27-01-83 12-07-83 16-07-85 31-10-90 11-01-90 14-02-83 18-03-86
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WO 9109989 A	11-07-91	AU 7051391 A CA 2070288 A DE 69007124 D EP 0506793 A JP 5504057 T	24-07-91 22-06-91 07-04-94 07-10-92 01-07-93
WO 9515821 A	15-06-95	US 5447565 A AU 1303795 A	05-09-95 27-06-95
WO 9623423 A	08-08-96	US 5496574 A US 5580593 A AU 4715396 A	05-03-96 03-12-96 21-08-96